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PARTICULATE EMISSIONS FROM PROTOTYPE CATALYST CARS

Morton Beltzer

Exxon Research and Engineering Company

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Particulate emissions from a vehicle equipped with a variety of commercial and prototype catalyst systems were measured and characterized. Nine catalysts including four monolithic and three pelleted oxidation catalysts and two NO_x reduction catalysts were screened on three test fuels over the 1975 FTP driving cycle and three study states. Particulate emissions increased due to the formation of sulfuric acid from exhaust SO_2. This sulfuric acid together with bound water accounted for most of the particulate emitted. Sulfate was the only form of sulfur detected in the particulate. Substantial differences between oxidation catalysts in their sulfuric acid formation tendency were detected. Additional information on the particle size distribution and metals content of the particulate is included.

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SUMMARY

A program to measure and characterize exhaust particulate emissions from a vehicle equipped with a variety of commercial and prototype catalyst systems was carried out. Nine catalysts (four monolithic oxidation catalysts, three pelletized oxidation catalysts, and two NO_x reduction catalysts) were screened on three test fuels. The oxidation catalysts were representative of those used on 1975 production vehicles; the NO_x reduction catalysts, candidates for use in automotive emission control systems. The fuels used were an EPA-supplied reference fuel containing 21% aromatics, that fuel plus an additives package, and a 46% aromatics fuel with the additives package.

A rigorous conditioning procedure was carried out on both catalysts and the vehicle prior to emissions testing to minimize the effects of prior history on emissions. The vehicle was then operated through a series of cyclic and steady state tests on each of the three test fuels. Emission rates of CO, HC, NO_x, and SO_2 were measured in each test mode. Total particulate emission rates were measured using the CVS compatible exhaust particulate sampler developed at Exxon Research. Particulate samples were analyzed for sulfate, carbon, bound water, nine metals, organic nitrogenous compounds, and organic sulfur compounds.

The following results were obtained with oxidation catalysts:

- Total particulate emission rates increased due to the production of sulfuric acid aerosol by catalytic oxidation of exhaust SO_2. This sulfuric acid aerosol and its associated bound water, was the major component of the particulate emitted. As a result, total particulate emission rate varied approximately linearly with fuel sulfur content. By contrast, particulate emissions from the vehicle without catalysts were independent of fuel sulfur level.

- The mass median equivalent diameter of catalyst exhaust particulate decreased relative to the non-catalyst case because submicron sulfuric acid aerosol was the predominant component of the particulate.

- Preliminary results of sulfate storage experiments indicate that released sulfate may have a larger particle size than sulfate produced during a run. Under certain conditions, the quantity of stored sulfate released may be several times that of freshly produced emitted sulfate. The emitted sulfate after storage conditioning may have two particle size distributions such that stored sulfate has a larger mass median equivalent diameter than freshly produced emitted sulfate. Further work is needed to substantiate these results.

- Pelletized catalysts store sulfate during certain test modes. Release of this stored sulfate can persist for several test runs, resulting in sulfate yields considerably in excess of 100% based on the sulfur in the fuel consumed.

- The differences in particulate carbon content between conventional and catalyst-equipped vehicles were smaller than expected, particularly under cyclic operating conditions, possibly because the presence of an air pump on the conventional vehicle lowered particulate carbon emissions. The carbon emission rates for oxidation catalyst equipped vehicles operating on 0.019 wt.% sulfur fuel ranged from zero to 0.019 gms/km and averaged about 30% of the total particulate. Carbon emission rates were independent of fuel sulfur content, the relative contribution of this particulate component decreasing with increasing fuel sulfur content.

- The emission rate of some metals was raised as a result of oxidation catalysts. The increment was not enough to influence total particulate emissions.

  - Aluminum emissions were higher, increasing from about 5 x 10^{-5} gms/km for the conventional vehicle to rates occasionally as high as 4.5 x 10^{-4} gms/km. The increase may be due to a low level of catalyst attrition.

  - Iron emissions were substantially higher, increasing from about 10^{-3} gms/km for the conventional vehicle to rates exceeding 5 x 10^{-3} gms/km for oxidation catalyst equipped vehicles. The increased iron emissions are probably due to reaction between the sulfate formed over the catalyst and the exhaust system. Iron emissions were independent of the amount of sulfuric acid emitted indicating that the reaction was wall (iron) limited.

  - Zinc emissions also increased. The source of the zinc was not determined.

  - Platinum was not detected in the exhaust particulate indicating that the emission rate must be below 5 x 10^{-6} gms/km.

With NO_x reduction catalysts, it was found that:

- Particle size distribution of the emitted particulate resembles that of a non-catalyst car, if conditions are not leaner than stoichiometric, when sulfuric acid aerosol is formed. In the latter case, mass median equivalent diameter is similar to that of an oxidation catalyst-equipped vehicle.

- Nickel emission rates with a Gould NO_x reduction catalyst equipped vehicle were as high as 2 x 10^{-3} gms/km. With a conventional vehicle or an oxidation catalyst equipped vehicle, nickel emission rates averaged about 2 x 10^{-4} gms/km. However, the increased nickel emission rates obtained with the NO_x reduction catalyst may have been due to improper operation of the vehicle at stoichiometric or net lean A/F ratios.

The following results were found to be independent of whether the vehicle was operated with or without a catalyst:

- Calcium emission rates correlated with expected lubricating oil consumption rates. Calcium was not a significant exhaust particulate, the emission rate averaging about 1 x 10^{-4} gms/km.
- Leaded particulate emission rates for the unequipped and catalyst-equipped vehicle were similar and were equivalent to about 50% of the lead burned.
- No nitrogenous organic particulate matter, either additive or otherwise derived, was found.
- Sulfate was the only sulfur containing exhaust particulate found.
- Particulate emissions did not increase when the fuel aromatic content was increased from 21 to 46%, indicating that the carbon particulate emission rate was independent of fuel aromatic content.

The major effect of catalysts used for automotive emissions control on exhaust particulate emissions are the production of sulfuric acid aerosol, and some increase in metal derived emissions, mainly those containing iron. Sulfates and associated bound water are the predominant components of exhaust particulate, followed by minor quantities of organic particulate and metal derived particulate. The relative contributions of the latter two types of particulate decreases with increasing fuel sulfur content.

I. INTRODUCTION

Automotive particulate emissions are of concern because of the potentially deleterious effects to health as a result of their accumulation in the atmosphere. Particulates also reduce atmospheric visibility, are known to be the cause of increased soiling, and may also function as photosensitizers in smog forming reactions. In 1975, approximately 75% of the cars produced will be equipped with oxidation catalysts in order to control carbon monoxide and hydrocarbon emissions. In addition to reducing these pollutants, prototype systems were also shown to have further beneficial results, namely the reduction of unregulated emissions such as aldehydes, reactive hydrocarbons(1), and polynuclear aromatic hydrocarbons(2) to extremely low levels.

Particulate emissions from catalyst equipped vehicles however could differ markedly from that of conventional vehicles. For example, thermal and mechanical stresses of the catalyst and/or substrate could result in the presence of these materials in vehicular exhaust. Chemical conversion of catalyst and substrate material to a mobile condensed phase is another possible route for these materials to show up in vehicular exhaust. Finally, catalytic conversion of gaseous exhaust components to particulate matter could produce new exhaust components, not normally present in the exhaust of conventional vehicles. Sulfate aerosol is an example of a catalytically produced exhaust component not normally present in significant quantities in exhaust from conventional vehicles. This aerosol is produced by the catalytic oxidation of exhaust sulfur dioxide.

This report describes the first phase of a contract work program to study particulate emissions from catalyst equipped vehicles The major objectives of this program are the measurements and characterization of exhaust particulate emissions from a variety of catalyst systems (commercial and prototype) that may be used in automotive emission control. To this end, it was necessary to measure and characterize particulate emissions from vehicles in their conventional configuration prior to equipping them with catalysts in order to distinguish between vehicle and catalyst effect on total particulate emissions.

The first phase of this contract work was primarily a catalyst screening program. The catalysts selected for testing were those most likely to be used in commercial vehicles. Nine catalyst systems (four monolithic oxidation catalysts, three beaded oxidation catalysts, and two NO_x reduction catalysts) were tested with three fuels.

The three fuels used were a reference fuel supplied by EPA, that same fuel with an additive package, and a high aromatic fuel which also contained the additive package. This fuel selection was made so that exhaust particulate could be characterized as follows:

(1) level and composition of exhaust particulate from the use of an additive-free fuel in conventional and catalyst equipped vehicles,

(2) effect of fuel additives on particulate emissions from conventional and catalyst equipped vehicles,

(3) effect of a high aromatic fuel containing additives on particulate emissions from conventional and catalyst equipped vehicles.

Two matched 1974 - 350 CID (5.735 liter) Chevrolet V-8 vehicles equipped with air pumps and exhaust manifold air injection systems were used. One vehicle was used for all the particulate emission measurements, the other for conditioning and aging the catalysts.

A rigorous conditioning schedule prior to testing was carried out since it has been shown that particulate emissions, particularly sulfate emissions, are a sensitive function of vehicle history. Each of the catalysts was mounted on the test vehicle and conditioned for 3218 km (2,000 miles) on a Mileage Accumulation Dynamometer (MAD) over the Federal Durability Cycle using an eight-hour on, eight-hour off sequence. The conditioning fuel was different from the test fuel because of limited supply of test fuels. Prior to testing with a given fuel, the vehicle was operated on that fuel for 200 miles on the MAD using the Federal Durability Cycle, followed by a sixteen-hour cold soak.

The vehicle was then operated through the following series of tests on each of the three test fuels:

(1) 1975 FTP
(2) One hour idle
(3) One hour, 64 km/hr (40 mph) cruise
(4) Two hour, 113 km/hr (70 mph) cruise or a two hour, 96 km/hr (60 mph) cruise
(5) Overnight soak
(6) 1975 FTP

Gaseous emission rates (CO, hydrocarbon, NO_x, and SO_2) were measured in each test. Total particulate emission rates were measured in each test using the CVS compatible exhaust particulate sampler developed at Exxon (3).

Analyses of the particulate samples were carried out to determine the emission rates of the following:

Sulfate
Carbon
Calcium
Aluminum
Zinc
Chromium

Iron
Copper
Nickel
Lead
Platinum
Bound Water

Chemical analysis was carried out to determine the presence of non-sulfate sulfur particulate matter and for the presence of nitrogenous organic matter in exhaust particulate. Particulate size distribution determinations were carried out using an Anderson Particle Sizing Sampler.

II. TECHNICAL BACKGROUND

In this section, automotive particulate emissions will be briefly discussed, the exhaust particulate sampling system developed at Exxon will be described, as well as the capabilities of the sampling system.

II.1 Automotive Particulate Emissions

In this report, automotive particulate emissions are defined as any material, other than unbound water, emitted from a vehicle tailpipe which exists in the condensed state at 32°C (90°F), that is larger than a small molecule but less than 500 microns in diameter. Exxon Research has used this definition of exhaust particulate since it was used by EPA in a work statement of a 1972 Request for Proposal to "Design, Develop, Fabricate and Test a Device Compatible with the Constant Volume Sampling System which will Allow Simultaneous Measurement of Gaseous and Particulate Emissions from Light Duty Vehicles"(4).

II.2 Exhaust Particulate Sampling System

The exhaust particulate sampling system has been designed to collect particulate matter at constant temperature during the 1972 and 1975 Federal Test Procedure, and 64 km/hr (40 mph) cruise conditions. This system is capable of frequent and convenient operation, and is compatible with constant volume sampling (CVS) of auto exhaust. Compatibility is obtained because the particulate sampler requires only a small portion of the diluted exhaust, the major portion of the sample is available to the CVS system for the measurement of gaseous emissions. Conditions used in the measurement of exhaust particulate conform to those mandated by the Federal Test Procedures for gaseous emissions.

This sampling system uses a small tunnel which means that low dilution ratios are used, allowing gaseous emissions such as CO, hydrocarbons, NO_x and SO_2 to be measured accurately. While low dilution ratios are desirable from the standpoint of CVS gaseous emission measurements, the collection of a proportional sample of particulate matter at constant temperature 32°C (90°F) from a sample stream having a high dew point without causing condensation of water requires an advanced temperature control system.

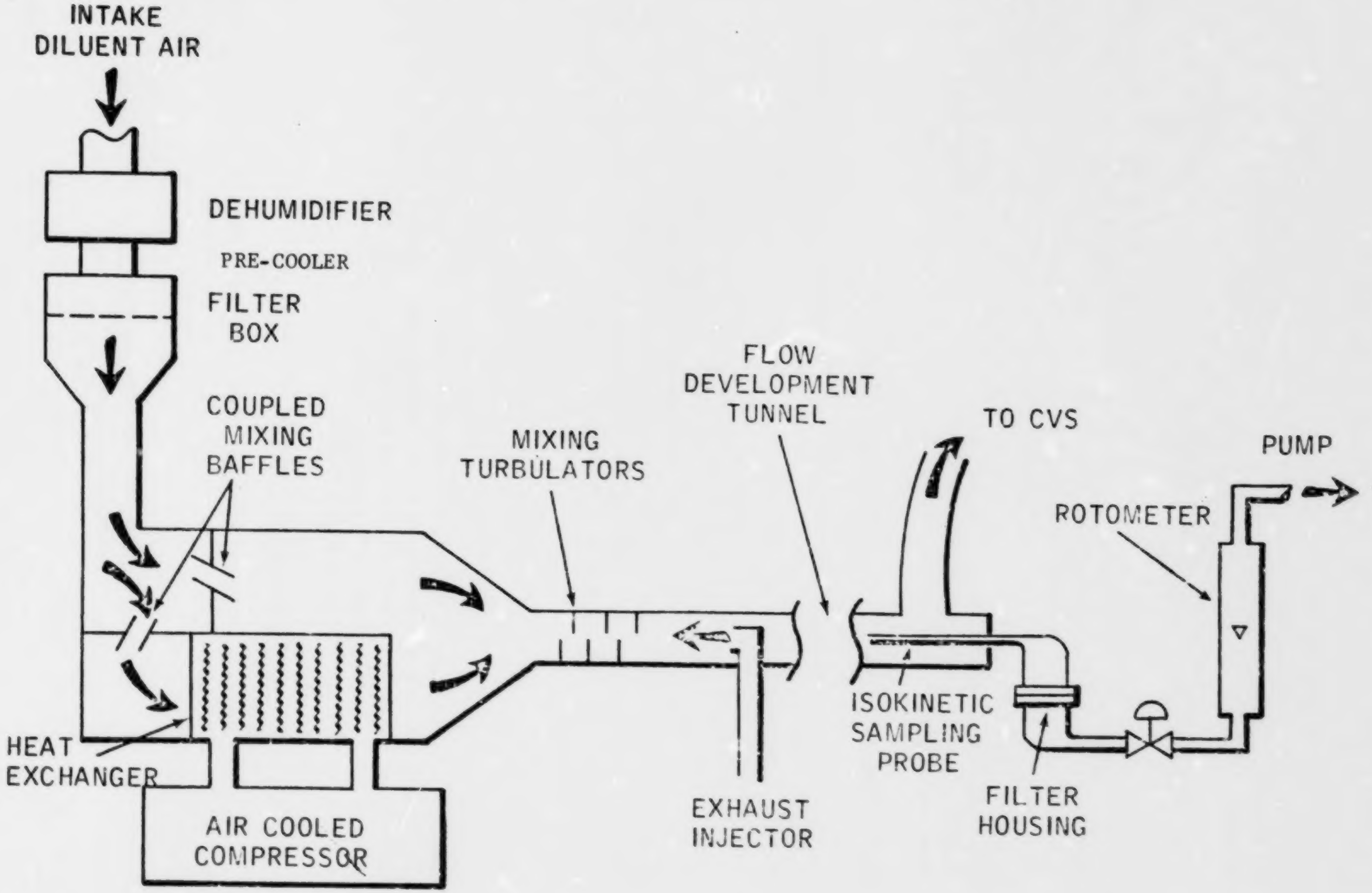
II.2.1 Sampling System Components

The particulate sampler which has been discussed previously(3,5) is shown schematically in Figure II-I. This system has five major components:

1. A diluent air preparation system
2. A flow development tunnel
3. An exhaust injector system
4. An isokinetic sampling probe
5. A particulate measuring device, which in the case shown is a 0.2 micron glass fiber filter

FIGURE II-1

EXHAUST PARTICULATE SAMPLER



The overall function of this system is to allow the collection of particulate matter from an isokinetically sampled portion of diluted exhaust which has been cooled to 90°F by dilution with chilled, dehumidified, filtered air. The function of each of the components in accomplishing this objective is described below.

II.2.1.1 Diluent Air Preparation System

This system consists of a dehumidifier, filter, coupled mixing baffles, a cooling system, and mixing turbulators.

The dehumidifier shown schematically in Figure II.2 minimizes the possibility of condensation occurring in the sampling system during a run, and is an integral part of the temperature control system. Diluent air is dried by passage through a filter and a slowly rotating desiccant wheel containing laminated flat and corrugated asbestos, impregnated with a regenerable desiccant, LiCl. Dehumidification of diluent air and desiccant reactivation are concurrent processes, so that dehumidification can be carried out on a continuous basis. The dehumidifier, a Honeycombe Model HC 750-EA is manufactured by Cargocaire Engineering Corporation is described in their Bulletin No. 07169(6).

Dehumidified inlet air passes from the dehumidifier to a filter box containing a paper filter, a bed of activated charcoal, and a second paper filter. This assembly is the standard filter box assembly for the Scott Research Constant Volume Sampler (CVS) unit. The filter assembly removes the particulate matter present in the diluent air and reduces and stabilizes the background hydrocarbon content of the diluent air.

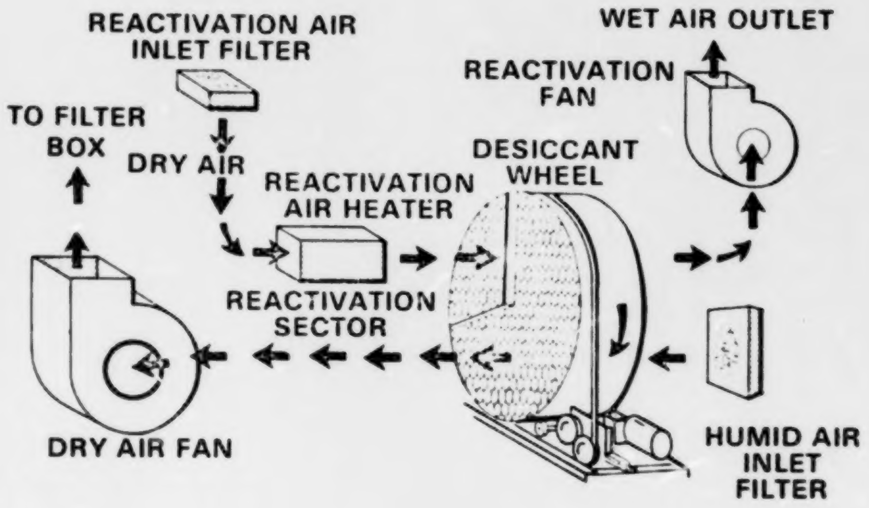
Because regeneration of the dessicant is accomplished by heating, the dehumidified air emerging from the drum is above ambient temperature. A pre-cooler situated between the dehumidifier and the CVS filter cools the dehumidified air stream down to ambient temperature to remove the additional cooling load imposed by the dehumidification step from the final cooling system. The pre-cooler consists of several rows of coils through which chilled city water is passed.

The coupled mixing baffles continuously divide the dehumidified, filtered air into two portions, one which passes through the cooling system, and a second portion which bypasses the cooling system. The position of the mixing baffles is controlled by a rapid response, deviation-type controller operating on an input signal from a thermocouple in the filter housing. The system is designed to maintain 90°F at the filter housing, during the 1972 or 1975 Federal Test Procedures, and 64 km/hr cruise.

The controller operates by comparing an input signal from a thermocouple in the filter housing with a set point signal, and takes corrective action to either raise or lower the output signal until the set point and thermocouple input are equal. The controller used was an Electronic Control System Model 6700 Controller(7). The output signal

FIGURE II-2

SCHEMATIC OF DEHUMIDIFICATION SECTION



from the controller is fed to an electric to pneumatic transducer (8) which in turn activates a pneumatic controller (9) which operates the coupled baffles.

The cooling system is an air cooled condensing evaporator which has a cooling capacity of 33,500 BTU/hour. The evaporator is a Dunham-Bush, Model SCO-50C unit(10) containing ten rows of custom-made cooling coils(11).

The mixing turbulators insure that chilled air is thoroughly mixed with the portion of air bypassing the cooling system before the stream is used to dilute the vehicle exhaust. The turbulators consist of six semi-circular perforated plates attached to a 1/2" diameter wall tube at their centers, arranged in a helical series sequence along the tunnel axis. This arrangement allows both longitudinal and latitudinal mixing.

Maximum flow through the diluent air preparation system is determined by the cooling capacity of the chiller. Presently, this limitation is 450 CFM.

II.2.1.2 Flow Development Tunnel

The exhaust and diluent air are mixed and a uniform velocity profile is developed in the flow development tunnel. The flow development tunnel is a 7.5 ft. long section of a 4-inch diameter Schedule 5 stainless steel pipe. Neither the length nor the diameter of the flow development tunnel have been optimized, but as will be shown in another section, a dilution tunnel of these dimensions is satisfactory for this purpose.

II.2.1.3 The Exhaust Injection System

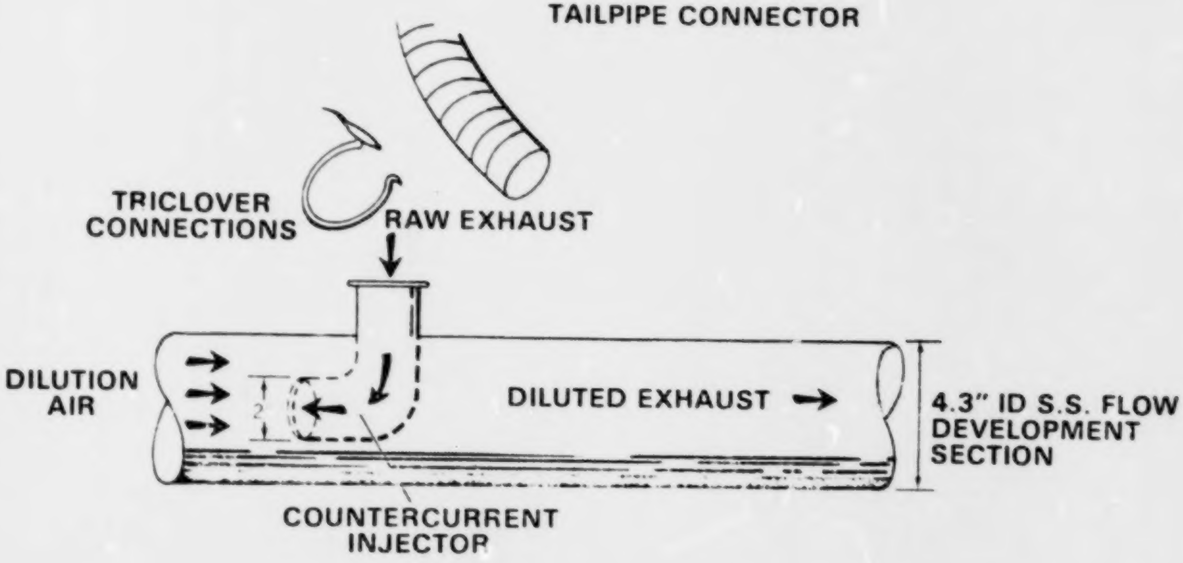
The raw exhaust is mixed with the diluent air normally used in the CVS in such a way as to completely mix the two in as short a time interval as possible. This is accomplished by injecting the exhaust in a countercurrent direction to the diluent air stream. Previous experiments(3) have shown this to be the most efficient way of obtaining a rapidly mixed, uniformly distributed diluted exhaust sample stream. Figure II-3 shows a schematic of the exhaust injector in the countercurrent position.

II.2.1.4 Isokinetic Probe

Isokinetic sampling is required to insure that the particulate sampled is representative of the particulate in the main stream; that is, the particulate concentration and size distribution in the probe sample should correspond to that of the main stream. The probes are designed so that the sample stream is divided into two parts with a volume ratio equal to the ratio of the cross-sectional areas of the openings of the sample probes and the tunnel cross-sectional area. Hence,

FIGURE II-3

COUNTER CURRENT EXHAUST INJECTION SYSTEM



$$\frac{\text{Area (probe)}}{\text{Area (tunnel)}} = \frac{\text{Flow Rate in SCFM (probe)}}{\text{Flow Rate in SCFM (tunnel)}}$$

Another problem to be considered in probe design is minimizing sample deposition in the probes. When suspended particulate matter leaves the tunnel and enters the sampling probe, it is leaving a low surface to volume region and entering a high surface to volume region. Relative sample losses by impaction should be greater in the probe than in the tunnel. Therefore, the probe should be as short and direct as possible to minimize the residence time of the particulate matter in the probe. The filter housing connected to the probe is flared out as soon as physically possible to minimize the surface to volume ratio of the housing and thereby reduce sampling losses by impaction in this portion of the sampling system.

II.2.1.5 Particulate Collecting Stage

At present, particulates are collected by filtering the sample through pre-weighed filters. In principle, other particulate collectors such as impactors and other devices, could be utilized with the particulate sampling system. In this paper, total particulates are determined gravimetrically using Gelman Type E glass fiber filters which have an effective pore size of 0.2 μ.

II.2.2 System Performance

In order to function properly, the exhaust particulate sampling system should have the following capabilities:

(1) Mix exhaust and diluent air rapidly.
(2) Allow development of a uniform velocity profile in the flow development tunnel.
(3) Minimize sampling losses in the tunnel.
(4) Give equivalent emission rates with parallel filters.
(5) Maintain constant temperature at the particulate collecting stage.

All of the above have been adequately documented (3,5) and will be reviewed in this section.

II.2.2.1 Rapid Mixing of Exhaust and Diluent Air

Three methods of injecting exhaust into diluent air were tested: co-current flow, perpendicular flow, and countercurrent flow. In each case, the exhaust was injected through a 2 in. O.D. x 0.035 in. wall stainless steel tube into the flow development tunnel. The efficiency of the three injection methods was tested by measuring hydrocarbon concentrations in the diluted exhaust at a point approximately 7.5 ft. downstream of the injection point. Hydrocarbons were chosen as the tracer because they are easier to measure than particulates. If the gaseous components of the exhaust are not evenly distributed over the flow cross-section, there is no reason to believe that the particulates will be well distributed. The ultimate test of uniformity of particulate distribution in the tunnel is the consistent attainment of equivalent particulate emission rates with parallel filters. **The results showed that uniform distribution was obtained only by countercurrent injection.**

II.2.2.2 Development of Uniform Flow in Flow Development Tunnel

To insure that samples taken at any point in the tunnel cross-section will contain the same amount of particulate material, a uniform radial distribution of particulate material in the tunnel must be obtained. The small size of the tunnel would make it difficult to obtain reliable measurements of velocity profiles. However, it is well known that the higher the Reynolds Number of turbulent flow, the flatter the velocity profile(12). However, over the range of interest for this system, the effect of this flattening of the velocity profile is negligible. Consider the system as having a flow of 450 SCFM of air at 90°F. through a 4.33 in. diameter pipe.

$$N_{Re} = \frac{D\overline{U}\rho}{\mu} \qquad (1)$$

where N_{Re} = Reynolds Number

D = pipe diameter = 4.34 in. = 0.361 ft

$\overline{U}$ = average fluid velocity = $\frac{4\,(450)}{\pi D^2}$ = 4395 ft/min = 2.64×10^5 ft/hr

ρ = density = 0.071 lb/ft

μ = fluid viscosity = 0.186 cp = 0.045 lb/ft-hr

$$N_{Re} \approx \frac{(0.361\ \text{ft})\ (2.64 \times 10^5\ \text{ft/hr})\ (0.71\ \text{lb/ft}^3)}{0.045\ \text{lb/ft-hr}} = 150{,}000$$

Equation (1) shows that the Reynolds Number varies inversely with diameter for constant volumetric flow. Therefore, decreasing pipe diameter to 1" would increase N_{Re} to 615,000 while increasing pipe diameter to 16" would decrease N_{Re} to 40,000.

One measure of the flatness of the velocity profile is the ratio of the mean gas velocity to the maximum gas velocity. It has been shown experimentally that for turbulent flow in smooth pipes(12)

$$\frac{u}{U} = \left(\frac{Y}{R}\right)^{1/N} \qquad (2)$$

where u = point velocity
U = maximum velocity at center
Y = distance from the wall
R = pipe radius, and
N = a constant depending on Reynolds Number

Schlicting (12) shows that average velocity $\overline{u}$ is,

$$\overline{u} = \frac{2N^2}{(N+1)(2N+1)} \qquad (3)$$

The following table shows that the effect of changing pipe diameter over a large range would be negligible.

Effect of Reynolds Number on Velocity Profile

N_{Re}	N	$\overline{u}/U$
23,000	6.6	.807
110,000	7.0	.816
500,000	8.0	.837

It should be noted that Schlicting's correlation is for a fully developed boundary layer which probably does not exist in the tunnel. Flow profiles are likely to be flatter than indicated above.

Another important factor in choosing the diameter of the flow development tunnel is its effect on the length of the tunnel and the diameter of the probes. As a general rule, ten pipe diameters are usually sufficient to develop a fully turbulent velocity profile. The larger the diameter, the longer the tunnel required and the longer the residence time in the flow development section. Longer residence time leads to higher particulate settling and greater inaccuracy in the measurement. Therefore, the tunnel diameter should be minimized. However, as tunnel diameter decreases, the pressure drop through the tunnel increases and the size of the probes needed for isokinetic sampling decreases. The problems caused by high pressure drop are obvious. Smaller diameter probes should be avoided since they provide higher surface to volume ratios and result in more loss of particulate by impaction. The 4.3 inch diameter pipe in use offers a reasonable compromise between these various factors.

II.2.2.3 Tunnel Sampling Losses

Particulate deposition in the flow development section was measured by introducing an artifically produced mono-disperse (3.5 micron diameter) methylene blue aerosol into the exhaust injector in the same manner as for auto exhaust. The system was disassembled after the run, the tunnel surface washed with methanol and the washings analyzed spectrophotometrically. The sensitivity of the method for methylene blue is in ppb range. Analysis showed that tunnel losses are small, amounting to less than 1% of the total aerosol introduced. No dye was detected in the tunnel section housing the exhaust injector. About

0.1% of the aerosol was deposited in the tunnel mid-section, and about 0.3% was deposited in the tunnel section housing the probes. Independent tests by U.S. Environmental Protection Agency workers with a tunnel of similar dimensions have confirmed our results regarding tunnel sampling losses(13).

II.2.2.4 Equivalent Emission Rates with Parallel Filters

Since only a small fraction of the diluted exhaust is sampled for the particulate analysis, at least two parallel probes coupled to the appropriate filters are needed to serve as internal checks on the sampling system. One method of determining whether proper sampling is achieved relies on the ratio of the weight of particulate collected (W_A) by filter A, and the volume flow rate (F_A) through probe A. This ratio should equal the corresponding ratio of these parameters for filter B and probe B, that is:

$$\frac{W_A}{F_A} = \frac{W_B}{F_B} = \frac{W_C}{F_C} = \text{etc.}$$

The particulate emission rates in grams/kilometer (gms/km) should be the same for all filters in a given run since

$$\frac{\text{gms}}{\text{km}} = \frac{W_A}{F_A}\left(\frac{F_P}{\Delta\text{km}}\right) = \frac{W_B}{F_B}\left(\frac{F_P}{\Delta\text{km}}\right) = \text{etc.}$$

where F_P is the volume flow rate through the tunnel and Δkm the distance in kilometers accumulated on the particular test procedure.

Excellent agreement between parallel filters has been obtained using this sampling system with conventional and catalyst equipped vehicles operating on a variety of unleaded fuels under cyclic and state test conditions. Partial documentation of this agreement has been previously described(3,5).

II.2.2.5 Temperature Maintenance of the Particulate Collection Stage

The dehumidifier is a key component of the temperature control system, particularly since the sampling system is one in which the air/exhaust dilution ratios are low, unlike other particulate sampling systems(14,15). This means that the relative humidity of the diluent air is a key parameter. For example, during the steep acceleration portion of the Federal Test Procedure, the exhaust volume flow rate from a vehicle equipped with a 350 CID V-8 engine may be as high as 120 CFM. This means that dilution ratio would drop below 3 in the sampling tunnel. If the relative humidity of the diluent air was high, attempts to control the filter temperature at 90°F would result in condensation of water vapor, with the associated loss of particulate matter. This is shown in Figure II-4 which depicts mixture dew point-dilution ratio dependence as a function of the relative humidity of the diluent (24°C) air.

The key role of the dehumidifier can readily be seen. If the relative humidity of the diluent air is low, e.g., below 50%, it should be possible to maintain a 32°C (90°F) filter temperature without condensation occurring. It can also be readily seen that in the absence of the dehumidifier, on humid days, the dew point of the mixture would exceed 32°C at dilution ratios as high as four, so that condensation would invariably occur during the acceleration portions of the driving cycle.

Attempts to control filter temperatures by omitting the dehumidification step and chilling the diluent air would be difficult to accomplish since water condensing on the coils would feed back latent heat, decreasing the efficiency of the cooler. Continued running would probably result in the condensed water freezing on the heat exchangers, rendering them inoperative.

Figure II-5 shows a typical trace of the relative humidity of the diluted exhaust in the vicinity of the sampling probes during FTP operation with a catalyst equipped vehicle. This trace is obtained by withdrawing a sample just above the sampling probes and filtering it prior to monitoring the humidity. Filtration is necessary in order to protect the rapidly responding humidity sensor(16).

It is evident that the relative humidity in the region of the probe closely parallels the changes in the cycle driving patterns. At no point in the driving cycle does the relative humidity at the probes reach the saturation level at 90°F. As the relative humidity is lower upstream, condensation in the tunnel upstream of the probe does not occur.

Figure II-6 shows the temperature-time trace at the filter during the above run which is a typical case. A total flow rate of about 450 SCFM was used. A four foot long 2 inch I.D. finned tube between the tailpipe and the exhaust injector was needed to suppress temperature spikes above 90°F during the steep acceleration portion of the driving cycle. It should be noted that the system is designed to prevent temperature excursions above 90°F, not to maintain that temperature during the course of the entire run.

FIGURE II-4

DEW POINT OF DILUTED EXHAUST VS. AIR/EXHAUST DILUTION RATIO

At Indicated Relative Humidities of 75°F (23.9°C) Dilution Air

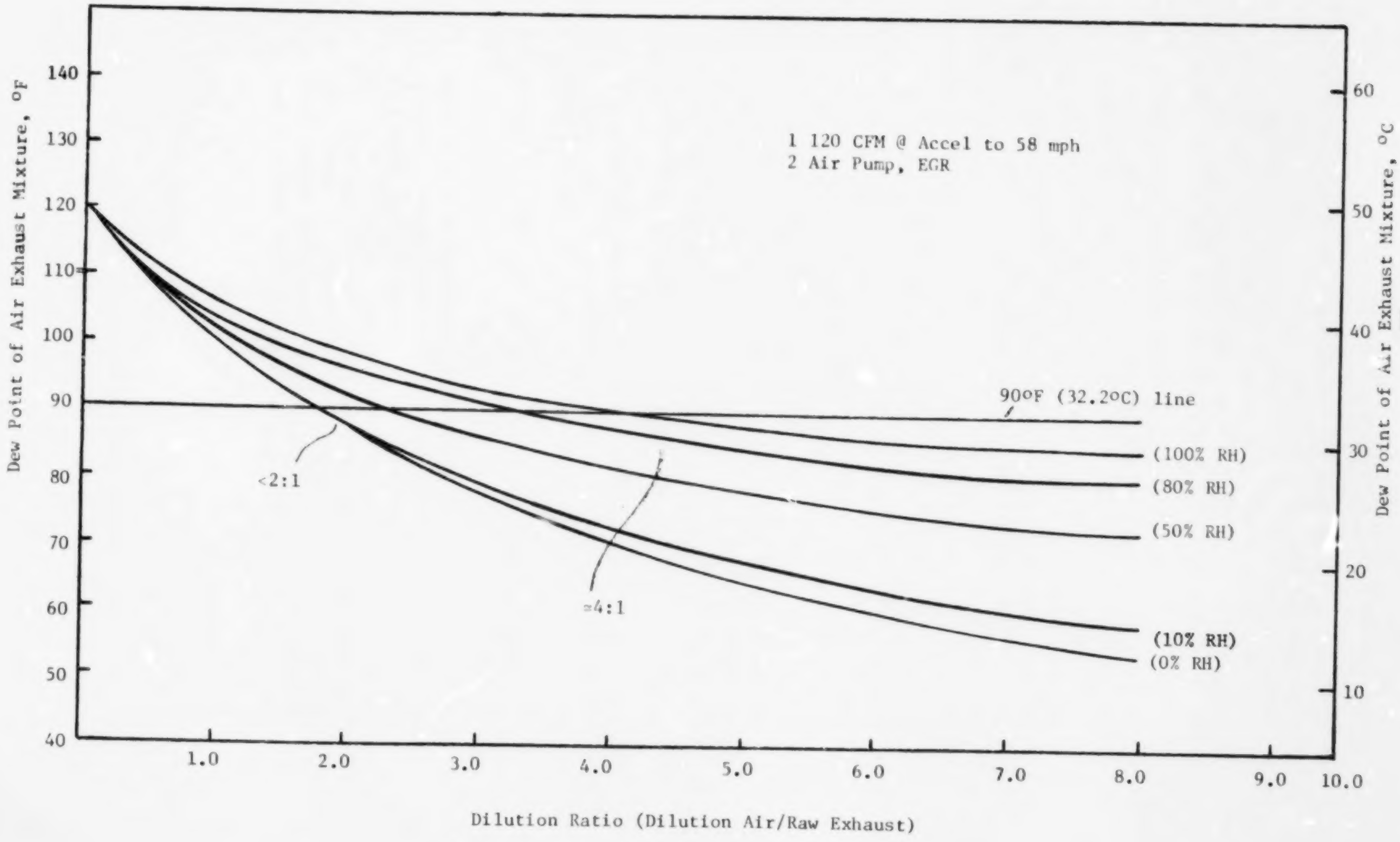


FIGURE II-5

RELATIVE HUMIDITY OF EXHAUST DILUTION AIR MIXTURE AT VICINITY OF SAMPLING PROBES DURING THE 1972 FEDERAL TEST—DRIVING CYCLE

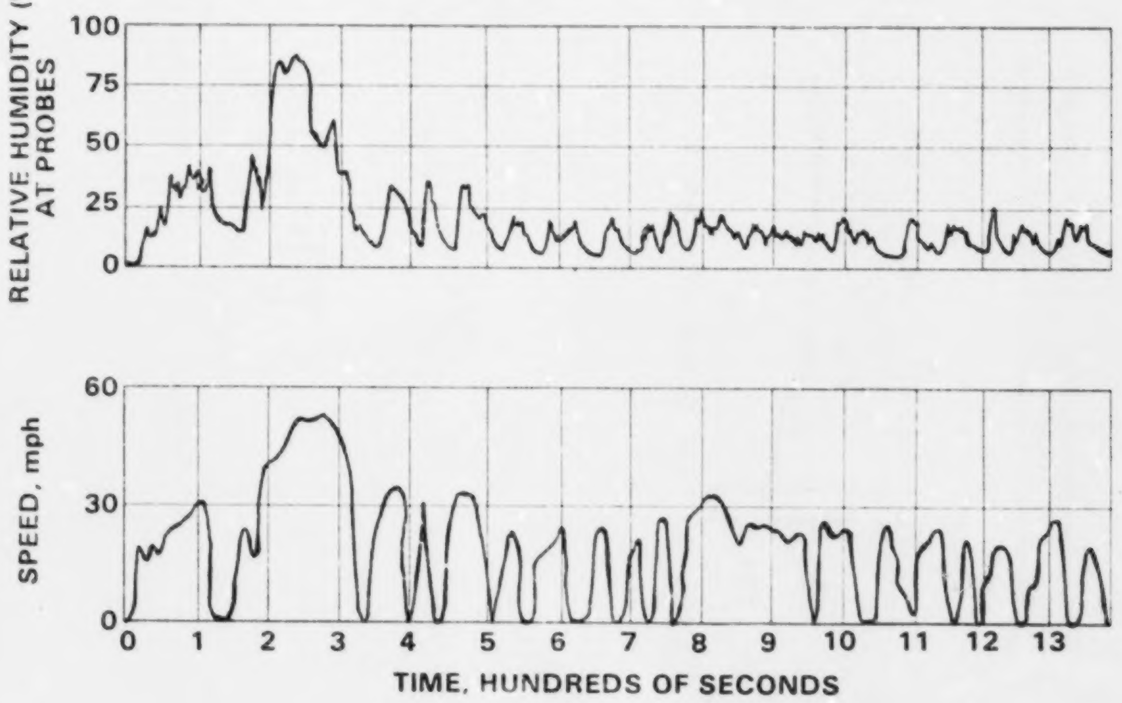


FIGURE II-6

TEMPERATURE CONTROL SYSTEM PERFORMANCE - CATALYST-EQUIPPED CAR

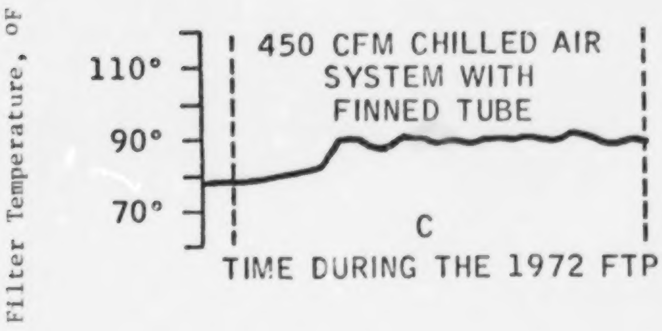


Figure II-7 is a typical relative humidity-time trace for a 40 mph steady state cruise experiment. The relative humidity surges to about 25% on start up and slowly decreases with running time.

Complete temperature control can be obtained at 40 mph by encapsulating the finned tube in a 4-inch diameter metal cylinder through which ambient air is pumped in a countercurrent direction to the flow of raw exhaust. Figure II-8 shows a schematic of this additional temperature control feature. Encapsulating the finned tube is not necessary for the driving cycle. At the 40 mph cruise, however, the temperature would slowly rise above 90°F after about 20 minutes if the finned tube was not encapsulated.

II.2.2.6 Capabilities for Studying Effect of Temperature on Particulate Collection

For the purposes of this work exhaust particulate matter is collected at 90°F. However, particulate can also be collected at other selected temperatures so that it would be useful for studying the effect of temperature on the quantity of particulate collected should the need arise.

This is because the set point temperature is essentially determined by the fraction of the dehumidified air that is cooled. If collection at a higher temperature is desired, the fraction of dehumidified air that goes through the heat exchanger is decreased. This fraction is determined by the set point temperature and the actual instantaneous temperature of the exhaust-dilution air mixture in the filter housing.

Thus a range of particulate collection temperatures is possible, the lower limit being the dew point of the air-exhaust mixture at the lowest dilution ratios, and the upper limit the minimum amount of cooled-dehumidified air required to prevent temperature increases, at low dilution ratios. To date, this range has not been investigated.

FIGURE II-7

RELATIVE HUMIDITY OF EXHAUST DILUTION AIR MIXTURE AT VICINITY OF SAMPLING PROBES DURING 64 kph CRUISE CONDITIONS at 32°C

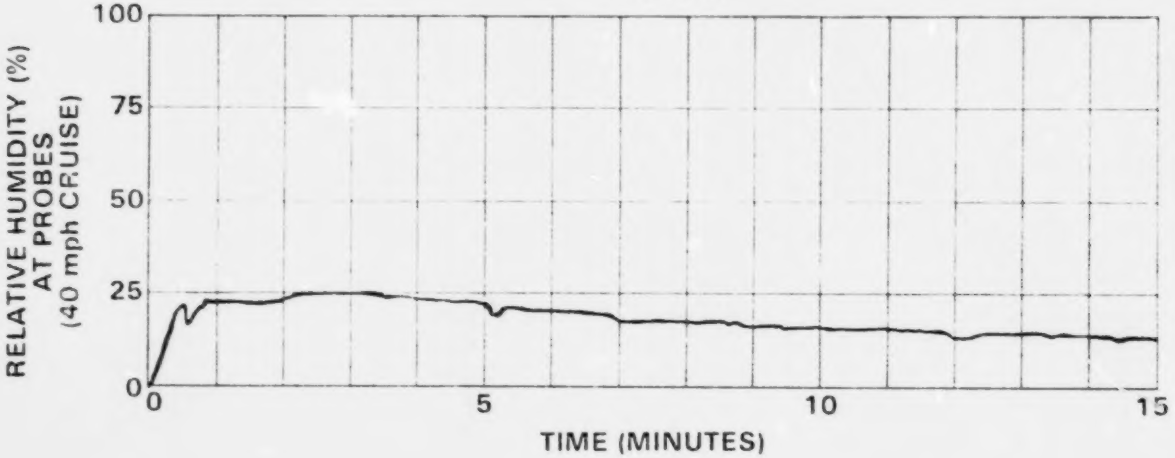
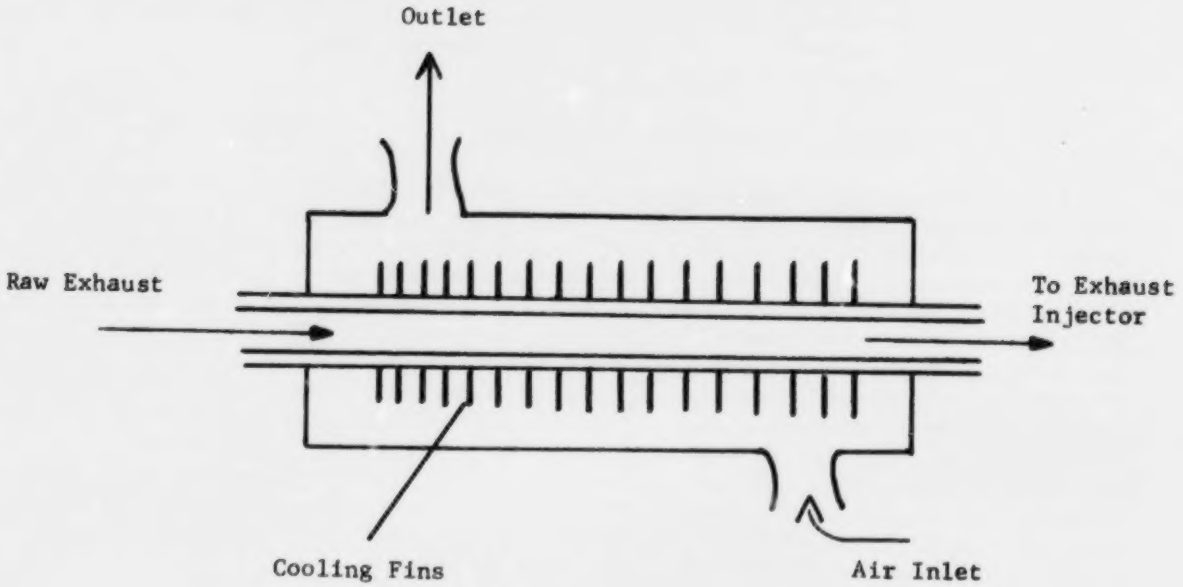


FIGURE II-8

FINNED TUBE COOLING SETUP



III. Experimental

III.1 Test Vehicles

Two matched 1974 350 CID Chevrolets were used in this program. These vehicles came equipped with air pumps and exhaust manifold air injection systems. The engine specifications listed below were set to manufacturer's specifications.

1974 Chevrolet 350 CID V-8

Spark plugs	.035 in.
Points dwell	30° ± 1
Basic Spark Timing	8° BTDC
Idle Speed	600 RPM, transmission in drive
Carburetor	Rochester 2 barrel, No. 7044114
Horsepower	145 at 3600 RPM
Compression Ratio	8.5:1

III.1.1 Vehicle Conditioning Procedures

Both project vehicles when received were drained of the leaded fuel contained in their fuel tanks. Their fuel systems were flushed to remove all traces of the factory fuel. Both vehicles were then driven by Exxon Research employees to accumulate about 3200 km ($\simeq$ 2000 miles) of commuter type mileage for initial break-in. The break-in fuel had a sulfur content of less than 100 ppm and a lead level of about 0.05 gm/gal. The specifications of the break-in fuel are given in Section III.2.2. To complete the break-in procedure, the vehicles were then operated for 3218 km on Exxon Research's automated Mileage Accumulation Dynamometer (MAD) using the Federal Mileage Accumulation Schedule (1). The 6400 kilometer accumulation had two purposes, to break in the vehicles, and to purge any traces of lead deposits that could have accumulated in the vehicle's combustion chambers and exhaust system over the few miles of vehicle operation during assembly and transportation.

Both vehicles were run through a complete set of particulate emission tests on all three test fuels to determine if there were any major differences between the two vehicles with respect to emissions (gaseous and particulate), and to establish base case engine particulate emission rates in order to separate vehicle and catalyst contributions to total particulate emissions.

One vehicle was then selected as the mileage accumulation vehicle, the other as the test vehicle. Both vehicles and all catalyst containers were fitted with quick disconnects to facilitate rapid interchange of catalyst systems between the mileage accumulation vehicle and the test vehicle. The test procedure will be discussed in Section III.4.

III.1.2 Catalyst Conditioning Procedures

All tests were initiated with the fresh catalysts mounted on the mileage accumulation vehicle in their proper position (post manifold or toeboard) depending on the catalyst configuration. The engine operating variables (carburetor adjustment, spark timing, points dwell, points gap and idle speed) were set according to the manufacturer's recommendations. Each vehicle was periodically tuned; after each catalyst break-in for the mileage accumulation vehicle, and after the battery of tests on a given catalyst for the test vehicle.

The mileage accumulation vehicle was operated on the MAD for about 2900 km (1800 miles) using the Federal Durability Driving Schedule and the mileage accumulation fuel. Mileage was accumulated on an eight hour on, eight hour off, basis to provide a cold start approximately once every 320 kilometers. The assumption was that this procedure would provide adequate thermal conditioning of the catalyst, and that the repeated cold starts would also subject the catalyst to some degree of thermal shock. After completion of the catalyst aging and conditions, the catalyst was transferred to the emission test vehicle and operated for 320 km (200 miles) using the Federal Durability Driving Schedule on the first test fuel to be used for particulate emission measurements.

The purpose of the 320 km accumulation was to equilibrate the catalyst with the test fuel. It was designed to eliminate any storage factors associated with the break-in fuel that could influence particulate emissions, so that these emissions would be truly reflective of the particular test fuel. It is quite probable that a 320 km accumulation is not of sufficient length to obtain equilibrium, but the time and fuel constraints placed on what is essentially a catalyst screening program in the first phase of this contract work did not allow operation for longer mileage in every test.

To more fully examine the storage problem, an additional test was made on a beaded oxidation catalyst system in which after following the normal test procedure, the catalyst-equipped vehicle was conditioned for an additional 6400 km (4000 miles) with one of the high sulfur test fuels to ascertain the effect of sulfate storage on particulate emissions. This additional test and the results obtained are discussed in Section IV.1.5.

Following the conditioning, the emission test vehicle was cold soaked for 16 to 24 hours prior to starting the particulate emission test procedure sequence. Control of the cold soak period allowed reproducible particulate emissions from the same vehicle.

After completion of the particulate emission measurement test sequence on a given fuel, the vehicle was returned to the MAD to accumulate 320 km using the second test fuel. After appropriate cold soaking and emission testing, the vehicle was again returned to the MAD to accumulate 320 km on the third test fuel. Emission measurements were made which completed the screening of that catalyst.

III.2 Selection of Fuels

The contract required that three fuels be used in the tests, a reference fuel supplied by EPA, that reference fuel plus an additives package, and a high aromatic fuel to be blended at the Exxon facilities, which contains the additive package. The aromatics level of the high aromatic fuel was selected on the basis of what the likely market place maximum would be.

III.2.1 The Additive Package

The contract required an additive package to be added to the EPA Reference Fuel and to the high aromatic fuel. The contents of this package were to contain the following:

- 0.05 g Pb/gal. as Motor Mix
- Additional sulfur as a mixture of thiophene and t-butyl disulfide to raise the sulfur content of the fuel to 0.1 wt. %.
- A nitrogenous multi-functional additive, and
- A heavy carrier oil or polymer type additive.

Lead as motor mix was added to achieve a level of approximately 0.05 gms/gallon. Sulfur was added as a mixture of 50% thiophene, 50% tertiary-butyl sulfide.

Lubrizol 596 (LZ596) was the nitrogenous multi-functional additive used. This additive, manufactured by the Lubrizol Corporation was used at the manufacturer's recommended maximum dosage, 25 lbs. per thousand barrels (0.27 g/gal.) LZ596 is a non-polymeric material containing 2.25-2.75% nitrogen by weight. It functions as a detergent, corrosion inhibitor, anti-stall agent, and anti-icing agent. Further details on the nature of this material are considered confidential by Lubrizol, but were filed with the EPA Air Pollution Control Office on April 28, 1971.

Paradyne 502 was used for the polymer type additive. This material, manufactured by the Exxon Chemical Company was used at the recommended dosage of 42 lbs. per thousand barrels (0.45 g/gal. Paradyne 502 is an approximately 3000 molecular weight polymer which contains

0.75% nitrogen by weight. It functions as a detergent, anti-rust agent and deposit modifier. As in the case of LZ 596, further details on the nature of this additive are confidential but are on file with the EPA Office of Air Pollution Control as of April 28, 1971

Because of the limited supply of test fuels for this program, a separate break in fuel for both vehicles and catalysts prior to testing was used. This fuel was to contain 0.05 gm Pb/gal. and less than 100 ppm sulfur, have normal volatility characteristics, and an octane level of at least 93 RON.

III.2.2 Fuel Specifications

Table III-1 shows the specifications of the break in fuel and the test fuels. Fuel (1) is the EPA reference fuel, fuel (2) that fuel spiked with the additive package, and fuel (3) the high aromatic fuel containing the additive package. Because of the dominant role of fuel sulfur content on exhaust particulate emissions, the test fuels will hereinafter be identified by their sulfur content such that:

Fuel (1) = 0.019 wt.% S
Fuel (2) = 0.110 wt.% S
Fuel (3) = 0.091 wt.% S

III.3 Catalysts

A total of 9 catalysts were tested. These include 4 monolithic oxidation catalysts, 3 pelletized oxidation catalysts and 2 NO_x reduction catalysts. The guidelines for catalyst selection were based on the probability of its commercial use in the near future and availability.

The following monolithic oxidation catalysts were tested:

(1) Engelhard PTX-IIB, hereinafter referred to as Engelhard Monolith.

(2) Two Universal Oil Products catalysts having ostensibly similar properties hereinafter referred to as UOP(1) and UOP(2) respectively.

(3) Matthey Bishop - hereinafter referred to as the Matthey Bishop Monolith.

Three pelletized oxidation catalysts were tested.

(1) Engelhard pelletized catalyst - hereinafter referred to as Engelhard Pellet.

(2) Grace pelletized catalyst - hereinafter referred to as Grace Pellet.

(3) Air Products pelletized catalyst - hereinafter referred to as Air Products Pellet.

Table III-1

Specifications of Fuels Used

	Break in Fuel	Fuel Designation (1)	(2)	(3)
ASTM Research Octane	95.5	93.0	92.6	98.8
ASTM Motor Octane	85.9	84.6	83.4	86.5
Lead (gms/gal)	0.052	<0.01	0.063	0.056
Weight % Sulfur	0.006	0.019	0.110	0.091
FIA Analysis				
% Aromatics	29.6	21.3	25.1	45.8
% Olefins	5.8	6.4	8.5	7.1
% Saturates	64.6	72.3	66.4	47.0
ASTM Gum (mg/100 ml)	0.4	0.0	0.0	4.4
RVP (psi)	8.32	9.4	8.58	8.64
API Gravity @ 60°F	61.1	60.5	59.6	52.2
ASTM Distillation (D86)				
IBP	94	92	95	100
5% Overhead at °F	120	115	117	125
10%	131	125	128	138
20%	149	143	149	160
30%	168	162	165	177
40%	190	183	190	203
50%	212	206	214	222
60%	229	223	233	248
70%	247	236	250	266
80%	271	251	274	297
90%	313	291	314	340
FBP	383	386	365	4.2
% Loss/% Bottoms	0.4/1.4	1.0/1.5	0.9/1.3	2.0/1.0

The two NO_x reduction catalyst systems were:

(1) Grace NO_x reduction catalyst - hereinafter referred to as Grace Reduction.

(2) GEM 68 catalyst made by Gould Inc. - hereinafter referred to as Gould Reduction.

The model and serial numbers of these systems where available are given in Table III-2 below.

Table III-2

Model and Serial Numbers of Catalysts Tested

Catalyst	Model Number	Serial Number
Engelhard Monolith	513	407 7011
UOP(1)	7471-210	
UOP(2)	7471-529	
Matthey Bishop Monolith		
Engelhard Pellet	8026	7-2916
Grace Pellet		
Air Products Pellet	260	HN 2428
Grace Reduction		
Gould Reduction		

III.4 Test Procedure

As discussed in the introduction section of this report, the test procedure consisted of operating a catalyst equipped vehicle through five separate modes: an initial 1975 FTP, followed by a one-hour idle, a one-hour 64 km/hr (40 mph) cruise, a two-hour 112 km/hr (70 mph) or two-hour 96 km/hr (60 mph) cruise. This was followed by an overnight cooling and a final 1975 FTP. The one-hour idle, and the two cruise modes were all hot start tests. No attempts to cool down between these tests were made.

Fresh, pre-weighed glass fiber filters were used in each test run to collect particulate for total particulate determination. A fresh (unweighed) Millipore filter was used in each run to collect particulate for metals analyses. Gaseous emission rates were determined in each test run for hydrocarbon, carbon monoxide, NO_x and SO_2 in diluted exhaust.

III.4.1 Gaseous Emissions

Since the exhaust particulate sampler is compatible with the CVS unit, simultaneous gaseous and particulate emission rates could be measured on each test mode. Carbon monoxide was analyzed using an NDIR analyzer, hydrocarbons by FID, NO_x by chemiluminescence and SO_2 by pulsed UV fluorescence. The measurement technique for SO_2 is discussed in detail in Section A.2 of Appendix A. The detailed gaseous emission rates are given in Appendix E.

III.4.2 Particulate Sampling Procedures

Four parallel filter samples were taken during each of the five test modes. These were as follows:

(a) Two 142 mm diameter Gelman Type A fiber glass filters coupled to probes sampling at 15 SCFM. These samples were used to check internal agreement and allow the determination of total particulate emission rates, sulfate emission rates, and for analyses of water, carbon, nitrogen, non-sulfate sulfur, and platinum. The analytical procedures for sulfate, water, carbon, etc., are discussed in Appendix A.

(b) One 90 mm diameter Millipore ashless filter coupled to a probe sampling at 5 SCFM. This filter sample was used for determination of the emission rates of Ca, Al, Zn, Cr, Fe, Cu, Ni, and Pb. All of these metals were determined by emission spectroscopy. This analytical technique and its adaption for measuring vehicular metallic emission rates is discussed in Section A.4 of Appendix A.

(c) A 1.5 SCFM sample for particulate size determination with an Andersen Particle Sizing Sampler. This sampler was modified to determine particle size distribution by weight. The use of the modified sampler is discussed in Appendix B.

. The Exhaust Particulate Sampler is designed to collect particulate emissions at constant temperature (32°C) during the FTP or 64 km/hr (40 mph) steady state cruise. However, the system was not designed to have the capability of handling the heat load generated by 96 km/hr (60 mph) and 113 km/hr (70 mph) cruise conditions. In order to maintain temperature control at the high speed cruise conditions, attempts were made to use a raw exhaust flow splitter. The function of this splitter was to reduce the heat load on the sampling system by venting a known constant fraction of raw exhaust prior to injection of the exhaust into the flow development tunnel. The splitter was designed to reject 75% of the raw exhaust.

Experiments with ambient air substituting for raw exhaust showed that the splitter worked as intended. However, the raw exhaust from an oxidation catalyst equipped vehicle corroded the velocity sensing elements of the device so that it was inoperable. The experiments with the exhaust splitter are described in Appendix C.

Consequently, the high speed cruise runs were carried out with the entire exhaust injected into the tunnel, which meant that particulate was not collected at constant temperature for these runs. This means that during the high speed cruises, deviations from isokinetic sampling occur. The error created by non-isokinetic (or anisokinetic) sampling has been studied by several investigators(2). For fine particles, less than 10 microns equivalent diameter, the error introduced by deviations from isokinetic sampling that are less than 20% are negligible. For coarse particles (greater than 50 microns equivalent diameter), the error in measuring particulate approximates the deviation from isokinetic sampling(26) The Environmental Protection Agency(27) has suggested that for deviations from isokinetic sampling of less than 20%, particulate mass be corrected by the equation

$$M = \frac{1}{2} M_S (1 + V_S/V)$$

where M = the actual mass of particulate
M_S = the mass of particulates in the sample
V_S = volumetric flow rate of the sample
V = volumetric flow rate of an isokinetic sample

The above equation indicates that the error in measuring the particulate mass will be half the deviation from isokinetic sample regardless of whether the sampling is supra or subisokinetic.

In the high speed cruises without temperature control, the deviation from isokinetic sampling through most of the run is below 10% so that the error in measuring the particulate mass is below 5%. This is the error caused in sampling particulate matter present in a stream above 32°C (90°F).

Another source of error caused by temperature excursions above 32°C is that organic matter that exists as particulate at that temperature and consequently is collected on the filters may not exist as particulate at the higher temperatures. This would apply to some of the organic components that would exist as particulate matter. There is no way of evaluating the error from this temperature effect, although it is probably small because of the following reason. The lean carburetion on both vehicles reduces not only the gaseous emissions but also the organic exhaust particulate components. These vehicles are also equipped with air pumps and exhaust manifold air injection to further decrease hydrocarbon and CO emissions by reaction of the oxygen in the air with the hot exhaust gases. At the high raw exhaust temperatures, air injection also reduces the gaseous organic precursors of organic particulate. Thus, the formation of organic particulate emission rate of a conventional 1974 GM vehicle should be considerably below that exhibitied by earlier vehicle models. Springer(28) presents evidence that with a 1970 Chevrolet CID V-8, the total particulate emission rate is very sensitive to temperature below 200°F. Based on Springer's data, it is estimated that at the maximum of the temperature excursion during the high speed cruise, the decrease in collected particulate would be approximately 16%. However, since it takes a finite time interval to approach the higher temperatures, the run averaged temperature effect on particulate losses should be below 16%.

It would also be expected that with the leaner operation of a 1974 vehicle coupled with air injection, only the less volatile, less easily oxidized organic precursors would be more likely to survive. The formation of these precursors into particulate matter would occur at high temperatures, so that their collection at filters would be less sensitive to collection temperature. Consequently, it would be expected that with the vehicles used in this program, the effect of temperature at the particulate collection stage on the organic particulate matter collected would be small enough to be within acceptable limits so that only small errors in calculated emission rates would result.

When the vehicle is equipped with an oxidation catalyst, the organic portion of the exhaust particulate is extensively reduced about an 80% reduction relative to pre-control vehicles, with the result that there is little temperature dependent organic particulate precrusors in the raw exhaust. Consequently, the effect of particulate collection temperature on organic particulate emissions should be quite small.

The collection of sulfuric acid aerosol should be independent of temperature as long as the collection temperature is below sulfuric acid dew point. Thus, if the collection temperature does not exceed about 90°C (29,30), all of the acid exists as aerosol. Although the tunnel residence time is small (≃0.1 second), the formation of aerosol droplets is virtually instantaneous(31). Particulate collection temperatures during the high speed cruises are well below the sulfuric acid dew point so that all the sulfuric acid exists as aerosol.

The collection of the metallic components in the exhaust particulate obviously are not temperature dependent so that no error in the measurement of these species occurs as a result of the temperature increases incurred during the high speed cruise modes.

IV. RESULTS AND DISCUSSION

IV.1 Sulfur Compounds in Exhaust Emissions

IV.1.1 SO_2 in Auto Exhaust

Although the charge of the contract was the characterization of exhaust particulate matter, the contract specified that 30 SO_2 measurements should be carried out. Sulfur dioxide determinations were performed in virtually every run however since this compound is not only the most predominant sulfur containing gaseous species in auto exhaust, but because particulate sulfate is derived from exhaust SO_2. Thus determination of exhaust SO_2 coupled with determination of particulate sulfate allows the determination of the fate of fuel sulfur, and the attainment or lack of a sulfur material balance allows one to approximately assess the extent of sulfate storage. The phenomenon of sulfate storage is discussed in Section IV.1.5. Sulfur dioxide was measured using the TECO pulsed fluorescence analyzer discussed in Appendix A.

Although other gaseous sulfur compounds may exist in auto exhaust, they are not related to particulate sulfur compounds (predominantly sulfate), and exist in quantities too small to have appreciable effects on sulfur material balance. The accounting of fuel sulfur in terms of emitted SO_2 and sulfate aerosol is discussed in Sections IV.1.4.1 and IV.1.4.2.

IV.1.2 Dependence of Total Particulate Emission Rates on Fuel Sulfur Content

Figure IV.1 shows the total particulate emission rates obtained on the averaged 1975 FTP's for the base case vehicle, and with the vehicle equipped with monolithic oxidation catalysts. It can be seen that with the unequipped vehicle, the total particulate emission rate is independent of the fuel sulfur content. With the monolithic oxidation catalysts, the total particulate emission rate is approximately linearly dependent on the fuel sulfur content.

Similar type of behavior was obtained when the vehicle was equipped with pelletized oxidation catalyst systems. However, the total particulate emission rates were lower than that obtained with monolithic oxidation catalysts, so that a lower order of dependence of emission rate on fuel sulfur content is observed as shown in Figure IV.2.

The average of the initial and final 1975 FTP total particulate emission rates (Figures IV-1 to IV-3) was used as a convenient parameter to approximately gauge the dependence of these emissions on fuel sulfur content for the base case and catalyst equipped vehicle. There is no rigorous basis for choosing this average. This is especially so since there are cases with both the monolithic and pelleted oxidation catalyst runs where large differences in the initial and final FTP total particulate emission rates were obtained, indicating that the vehicle-catalyst combination being tested was not stabilized with respect to particulate emissions. Sulfate storage in the pelleted oxidation catalyst equipped vehicle is an additional complicating factor. That the total particulate

FIGURE IV-1

DEPENDENCE OF TOTAL PARTICULATE EMISSION RATES, gms/km ON FUEL SULFUR CONTENT (AVERAGE OF INITIAL AND FINAL 1975 FTP)

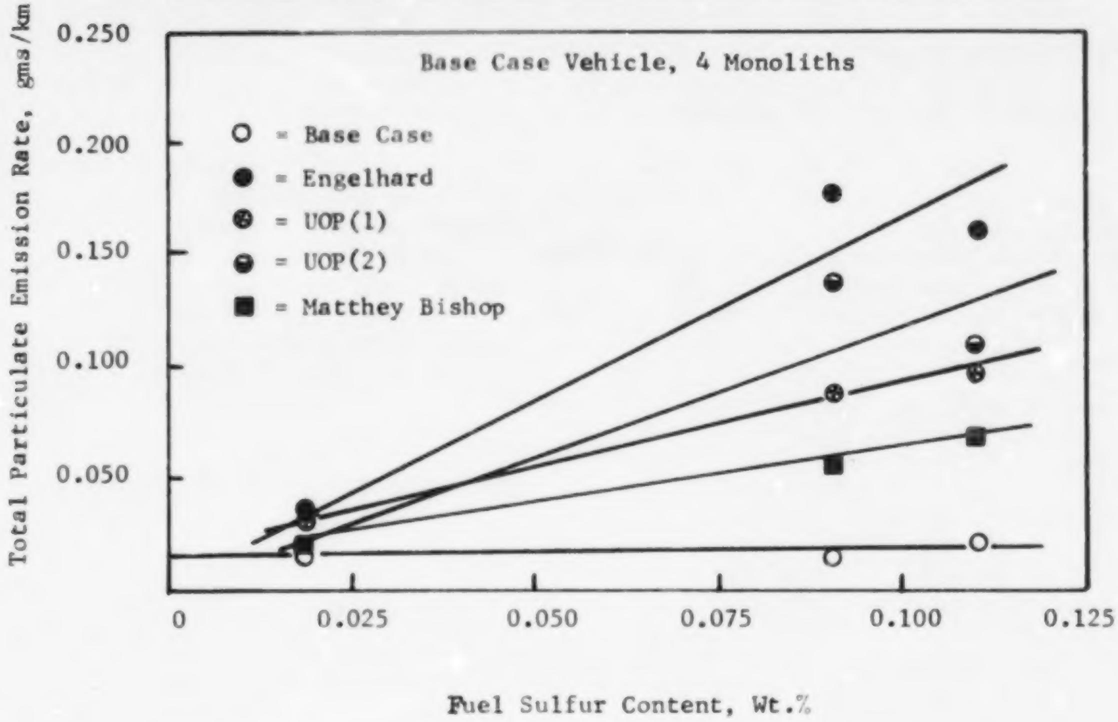
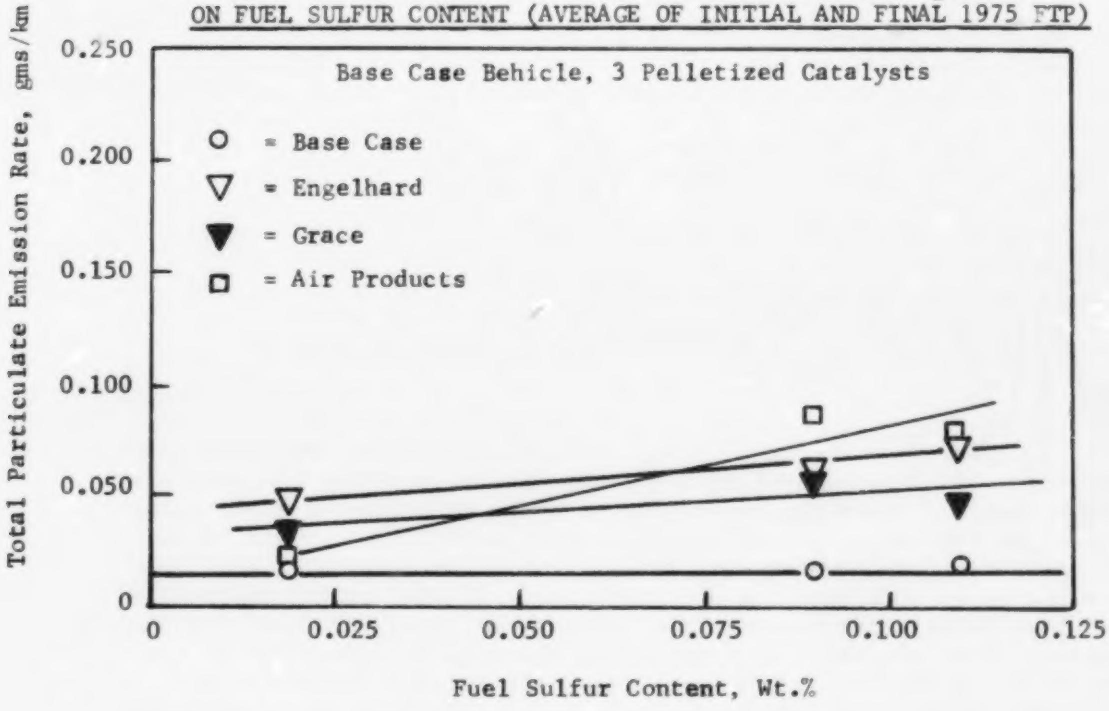


FIGURE IV-2

DEPENDENCE OF TOTAL PARTICULATE EMISSION RATES, gms/km ON FUEL SULFUR CONTENT (AVERAGE OF INITIAL AND FINAL 1975 FTP)



emission rates vary linearly with fuel sulfur content with oxidation catalyst equipped vehicles, Figures IV-1 and IV-2, may be fortuitous, at least for the FTP test runs. Thus, no theoretical significance should be attached to the slopes of the lines in Figures IV-1 and IV-2. While total particulate emission rates may vary linearly with fuel sulfur content with an oxidation catalyst equipped vehicle over a large variety of conditions, the case for linearity would best be substantiated with a thoroughly conditioned particulate emission stabilized test vehicle. This would be beyond the scope of this program. As stated previously, the intention of the plots in Figures IV-1 and IV-2 is to elicit the approximate dependence of particulate emissions and fuel sulfur levels as a function of catalyst type.

By contrast, the total particulate emission rates obtained when the test vehicle was equipped with NO_x reduction catalysts showed no dependence on fuel sulfur content. As shown in Figure IV.3, the particulate emission rates with NO_x reduction catalysts are essentially the same as with the base case vehicle.

On the 64 km/hr (40 mph) cruise runs, the total particulate emission rates with the unequipped vehicle were low and independent of fuel sulfur content. The total particulate emission rates with monolithic catalyst equipped vehicles were linearly dependent on fuel sulfur levels, and were greater than what was exhibited on the 1975 Federal Test Procedures, Figure IV-4. It can be seen that significant differences in the emission rates are exhibited by the monolithic systems tested, the UOP catalysts emitting about four times as much exhaust particulate as the Matthey Bishop catalyst. Similarly with the pelleted oxidation catalysts, as shown in Figure IV-5, total particulate emission rates also varied linearly with fuel sulfur content. The emission rates with the pelleted systems were lower than those of the monolithic systems, the exception being the monolithic Matthey Bishop catalyst.

As shown previously in Figure IV-3, the particulate emission rates of NO_x reduction catalyst equipped vehicles were invariant with respect to fuel sulfur content. This was not the case when the vehicle equipped with these catalysts was operated at 64 km/hr for one hour. As shown in Figure IV-6, the total particulate emission rates vary linearly with fuel sulfur content as in the case of the oxidation catalysts. Total particulate emission rates with the NO_x reduction catalysts are lower than what was obtained with any of the oxidation catalysts (monolithic or pelleted type).

At the high speed cruises (96 or 113 km/hr), the total particulate emission rates of the vehicle equipped with the various monolithic catalysts were linearly proportional to fuel sulfur content, but were lower than that exhibited by the same catalysts or the same fuels at the lower vehicle cruise speeds. The relative particulate emissions of the catalysts is changed in that the second UOP monolith, which emitted lower levels of particulates than the first UOP monolith at 64 km/hr vehicle cruise speed, emitted higher level at the higher speed cruise. Both UOP monolith equipped vehicles emitted more particulate than when equipped with the Engelhard or Matthey Bishop monolith. These results are shown in Figure IV-7.

With pelleted oxidation catalysts, deviations from linearity are observed with the Engelhard and Air Products catalyst systems. Emission rates obtained with the Grace catalyst equipped vehicle

FIGURE IV-3

DEPENDENCE OF TOTAL PARTICULATE EMISSION RATES, gms/km ON FUEL SULFUR CONTENT (AVERAGE OF INITIAL AND FINAL 1975 FTP)

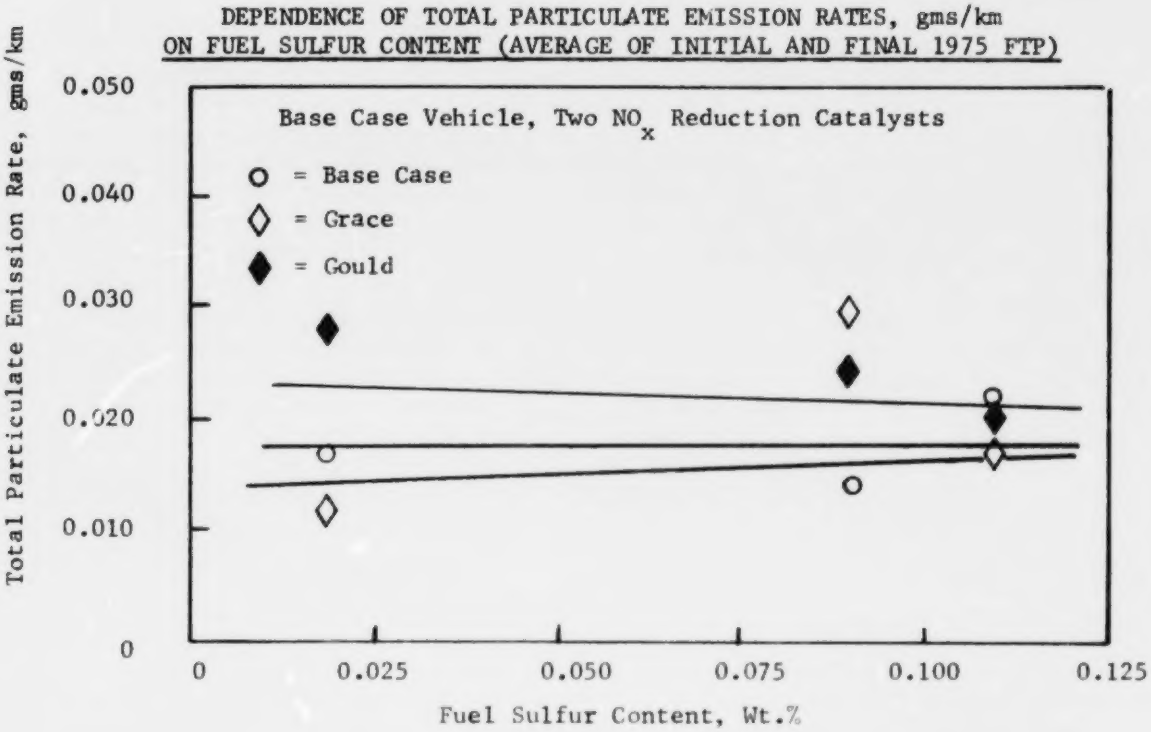


FIGURE IV-4

DEPENDENCE OF TOTAL PARTICULATE EMISSION RATES, gms/km ON FUEL SULFUR CONTENT MONOLITHIC CATALYST EQUIPPED VEHICLE

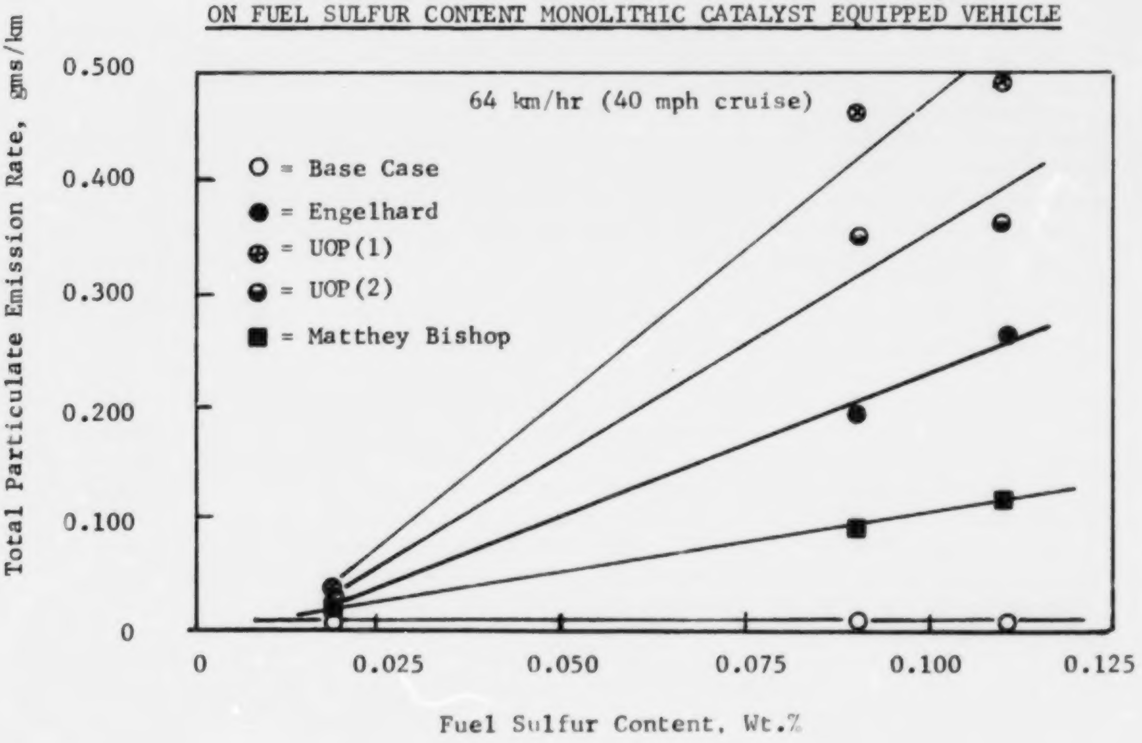


FIGURE IV-5

DEPENDENCE OF TOTAL PARTICULATE EMISSION RATES, gms/km ON FUEL SULFUR CONTENT, PELLETIZED CATALYSTS 64 km/hr (40 mph Cruise)

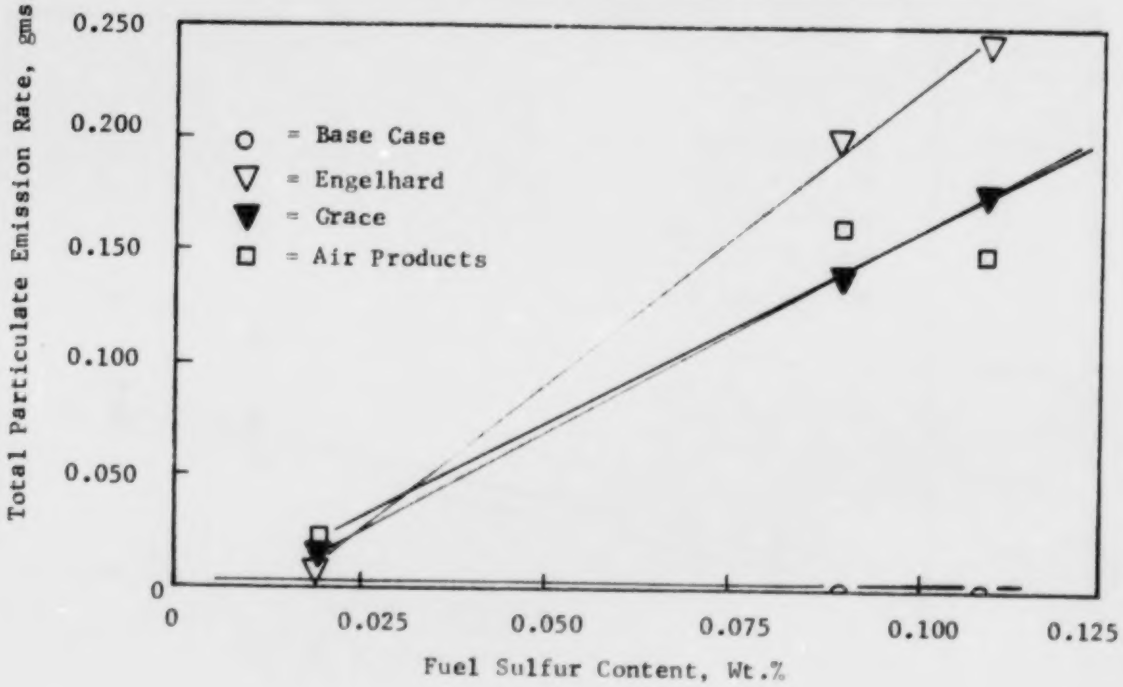


FIGURE IV-6

DEPENDENCE OF TOTAL PARTICULATE EMISSION RATES, gms/km ON FUEL SULFUR CONTENT WITH NO_x REDUCTION CATALYSTS 64 km/hr (40 mph Cruise

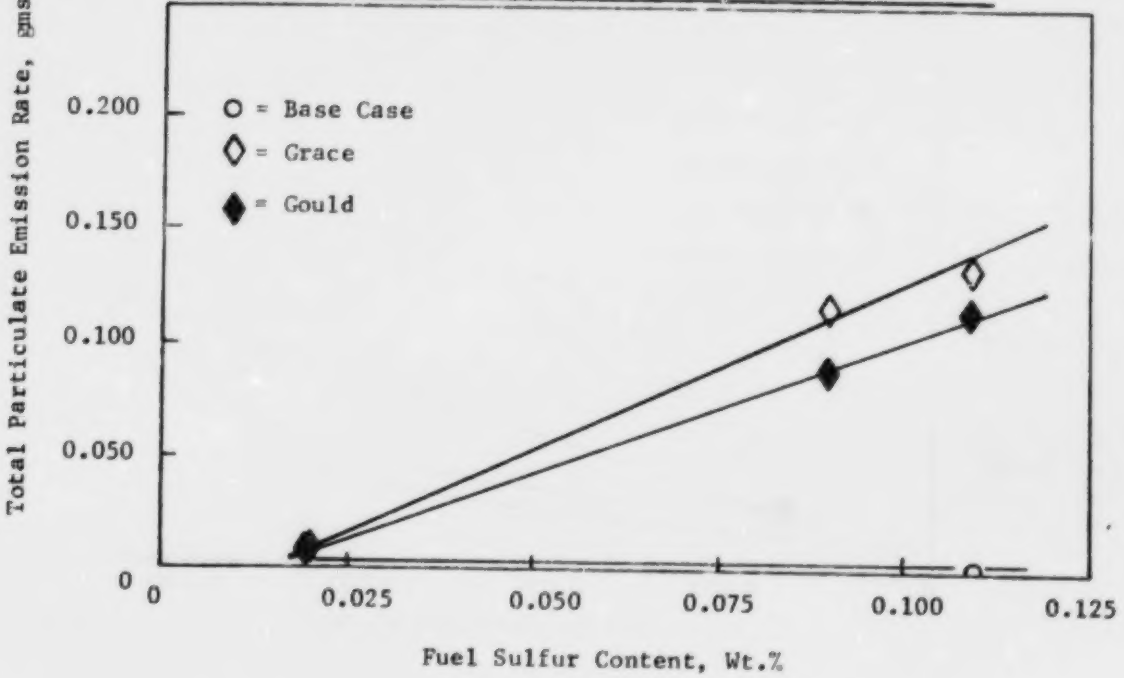


FIGURE IV-7

DEPENDENCE OF TOTAL PARTICULATE EMISSION RATES, gms/km ON FUEL SULFUR CONTENT MONOLITHIC CATALYST EQUIPPED VEHICLE (96 or 112 km/hr Cruise)

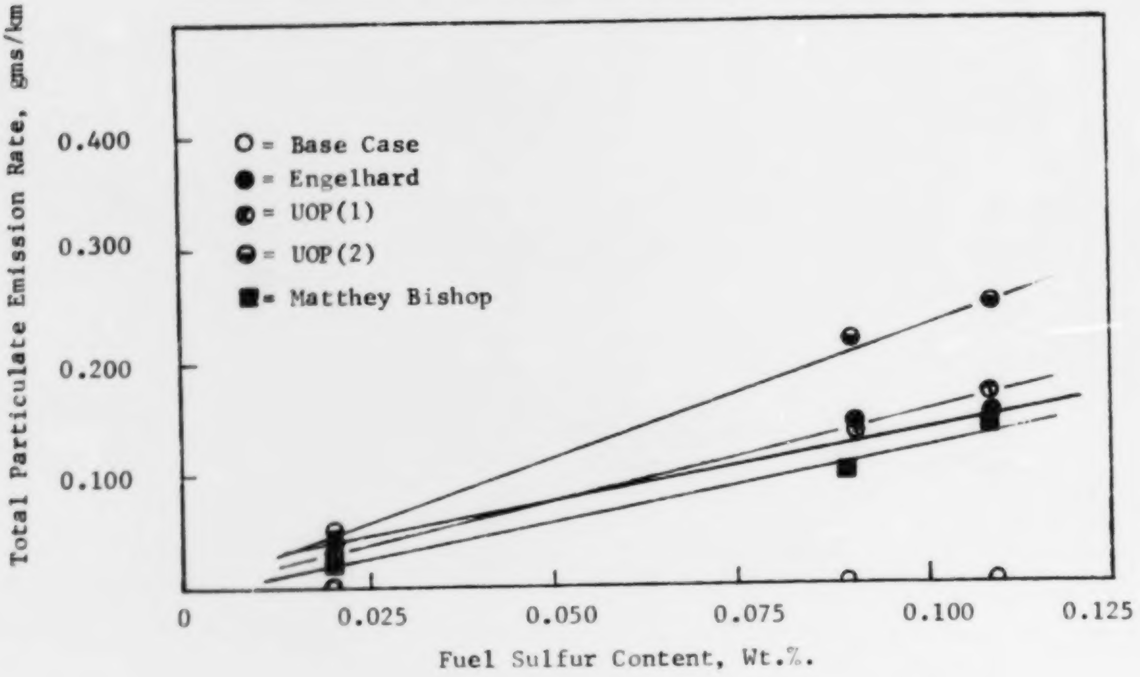
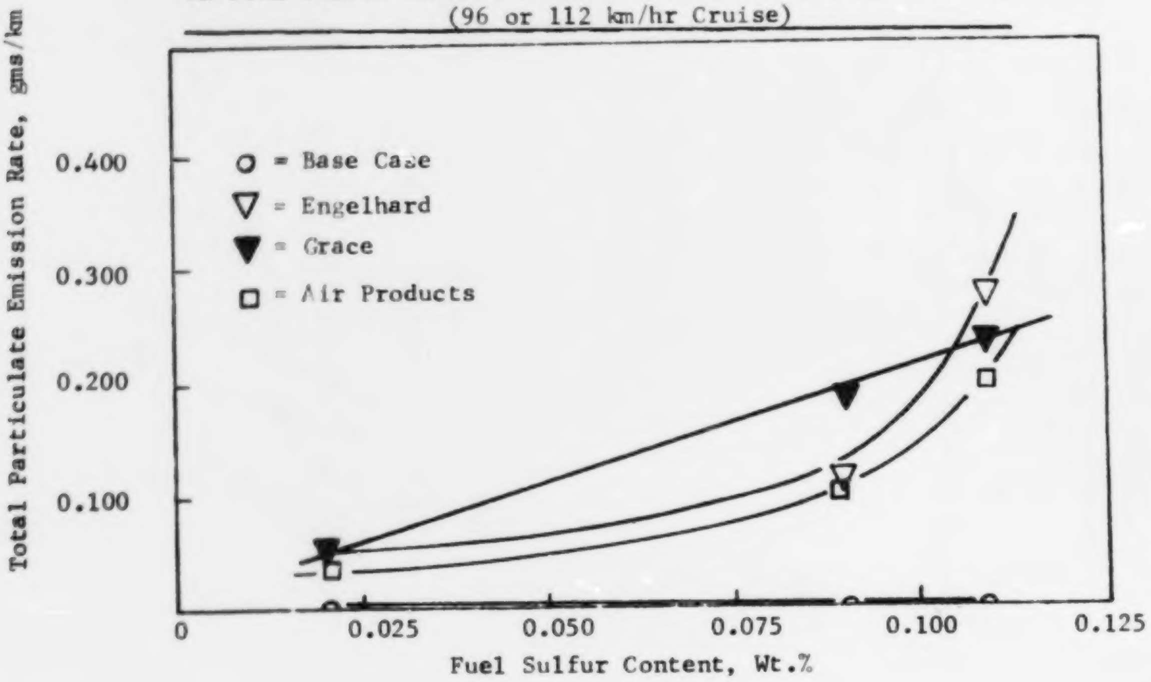


FIGURE IV-8

DEPENDENCE OF TOTAL PARTICULATE EMISSION RATES, gms/km ON FUEL SULFUR CONTENT PELLETED CATALYST EQUIPPED VEHICLE (96 or 112 km/hr Cruise)



varied linearly with fuel sulfur content. The high speed cruise results with the pelleted catalyst systems are shown in Figure IV-8. Figure IV-9 shows that the total particulate emissions varied linearly with fuel sulfur content at the high speed cruises when the vehicle was equipped with either the Grace or Gould NO_x reduction catalysts.

The dependence of the total particulate emission rates on the fuel sulfur content is due to the production of sulfate aerosol. This aerosol is produced in the presence of an oxidation catalyst, and under certain circumstances in the presence of a NO_x reduction catalyst. The presence of a heterogeneous catalyst is a necessary requirement. Sulfate production is discussed in the next section. The detailed data on total particulate emission rates are given in Appendix E.

IV.1.3 Sulfate Emission Rates

The quantity of soluble sulfate on the total filters was routinely determined using the titrimetric procedure discussed in Appendix A. Figure IV-10 shows the sulfate emission rates as a function of fuel sulfur content obtained on the 1975 FTP for the unequipped base case vehicle, and when the vehicle was equipped with each of the four monolithic oxidation catalysts. The sulfate emission rates are reasonably linear with fuel sulfur content as in the case of the total particulate emission rate. The slopes are about half that obtained on the total particulate plot. These results are consistent with earlier results(3) in which it was found that the sulfates emitted from an oxidation catalyst equipped vehicle account for approximately half the total particulate.

As shown in Figure IV-11, similar results are obtained with pelletized oxidation catalysts in that the emission rates of sulfate are approximately linear with fuel sulfur content and account for about half of the total particulate. The absolute levels of emitted sulfate for the pelleted catalyst equipped vehicles are generally lower than those obtained with a monolithic oxidation catalyst equipped vehicle. The differences exhibited between the monolithic and pelletized catalyst systems on the 1975 FTP can be attributed to storage of sulfate on the pelleted systems. Sulfate storage phenomenon are discussed in Section IV.1.5.

Figures IV-12 and IV-13 depict the sulfate emission dependence on fuel sulfur content for both monolithic and pelletized catalysts vehicles for the 64 km/hr cruises. In both cases, the sulfate emission rates vary linearly with fuel sulfur content. Sulfate emissions from the base case vehicle are too low to be sensibly plotted on the above figures.

The wide range of sulfate emissions for a given fuel sulfur level shown in Figure IV-12 indicates that significant differences exist between the various monolithic catalysts. For example, the vehicle equipped with the Matthey Bishop catalyst emitted only about one-fourth of the sulfate emitted with one of the UOP systems. It should be realized that only one sample of each catalyst was tested, replicate testing would be necessary to substantiate the observed differences. EPA (17), in their own tests, have corroborated the above results so that there is good reason to believe that the differences observed are significant. The sulfate emission rates with the pelleted catalysts are comparable to the Engelhard monolith and the second UOP monolith tested.

FIGURE IV-9

DEPENDENCE OF TOTAL PARTICULATE EMISSION RATES, gms/km ON FUEL SULFUR CONTENT, NO_x REDUCTION CATALYST EQUIPPED VEHICLE (96 km/hr Cruise)

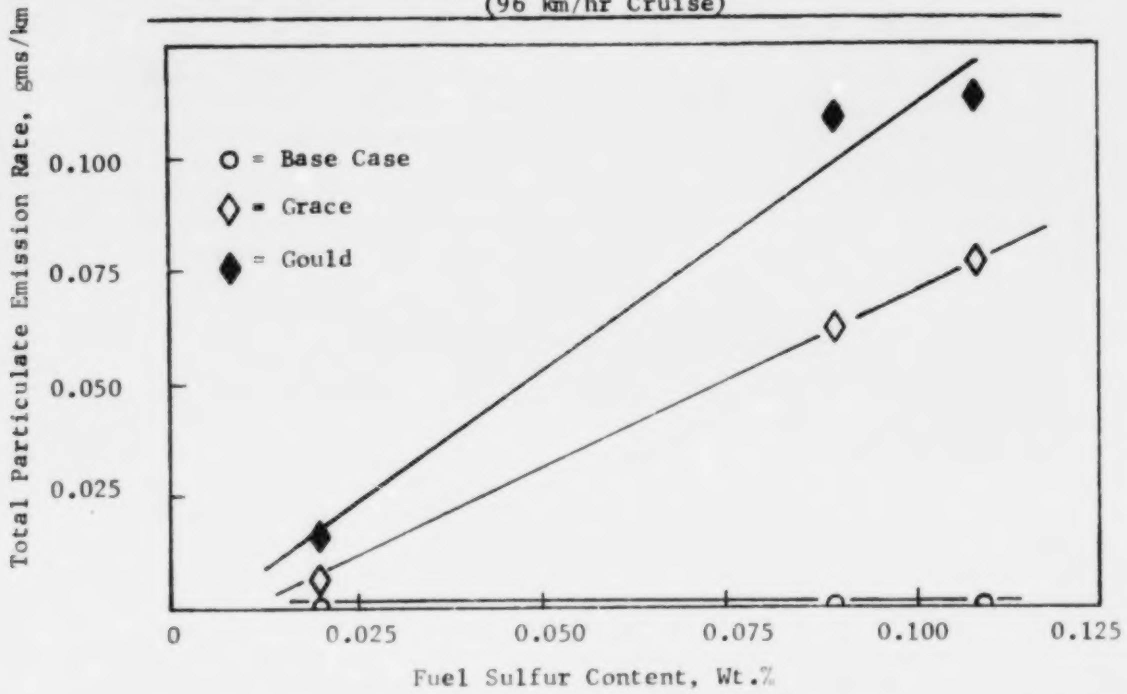


FIGURE IV-10

SULFATE EMISSION RATE VS. FUEL SULFUR CONTENT
(AVERAGE OF INITIAL AND FINAL 1975 FTP)
BASE CASE AND MONOLITHIC OXIDATION CATALYST EQUIPPED VEHICLE

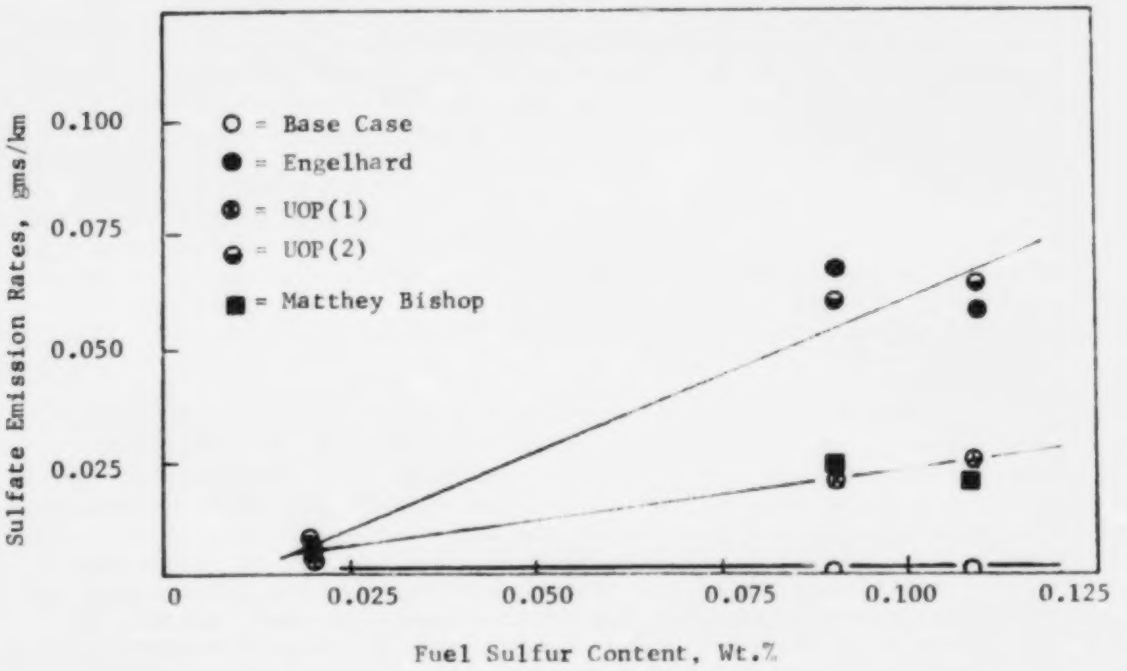


FIGURE IV-11

SULFATE EMISSION RATES VS. FUEL SULFUR CONTENT
(AVERAGE OF INITIAL AND FINAL 1975 FTP)
BASE CASE AND PELLETIZED OXIDATION CATALYSTS

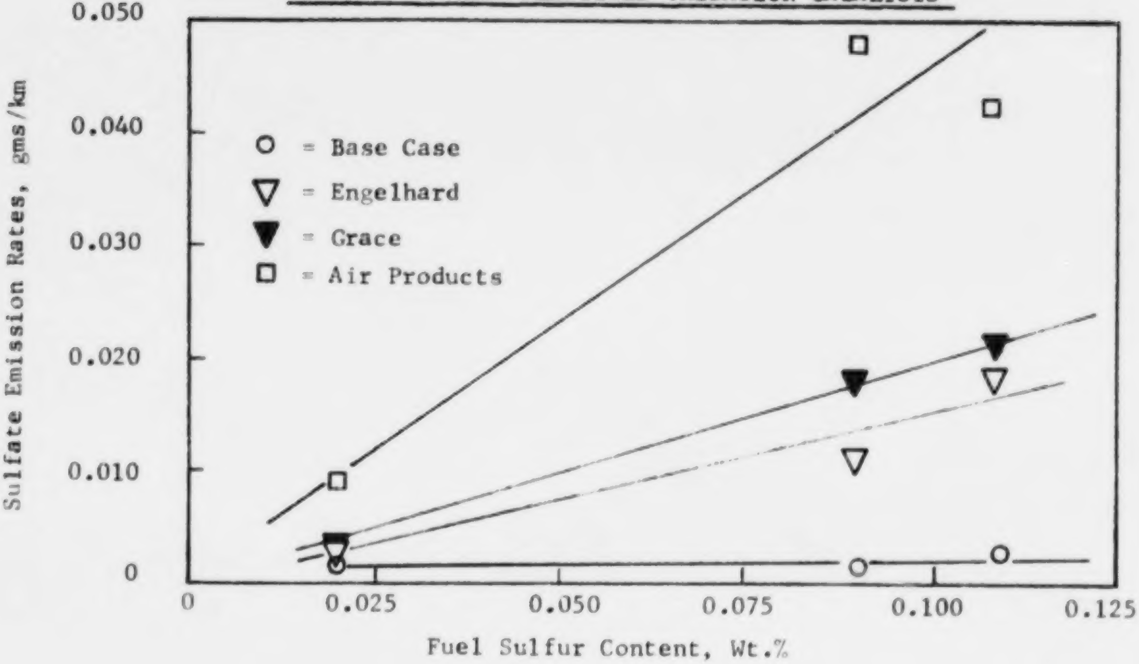


FIGURE IV-12

DEPENDENCE OF SULFATE EMISSION RATES, gms/km ON FUEL
SULFUR CONTENT MONOLITHIC CATALYST EQUIPPED VEHICLE
64 km/hr (40 mph Cruise)

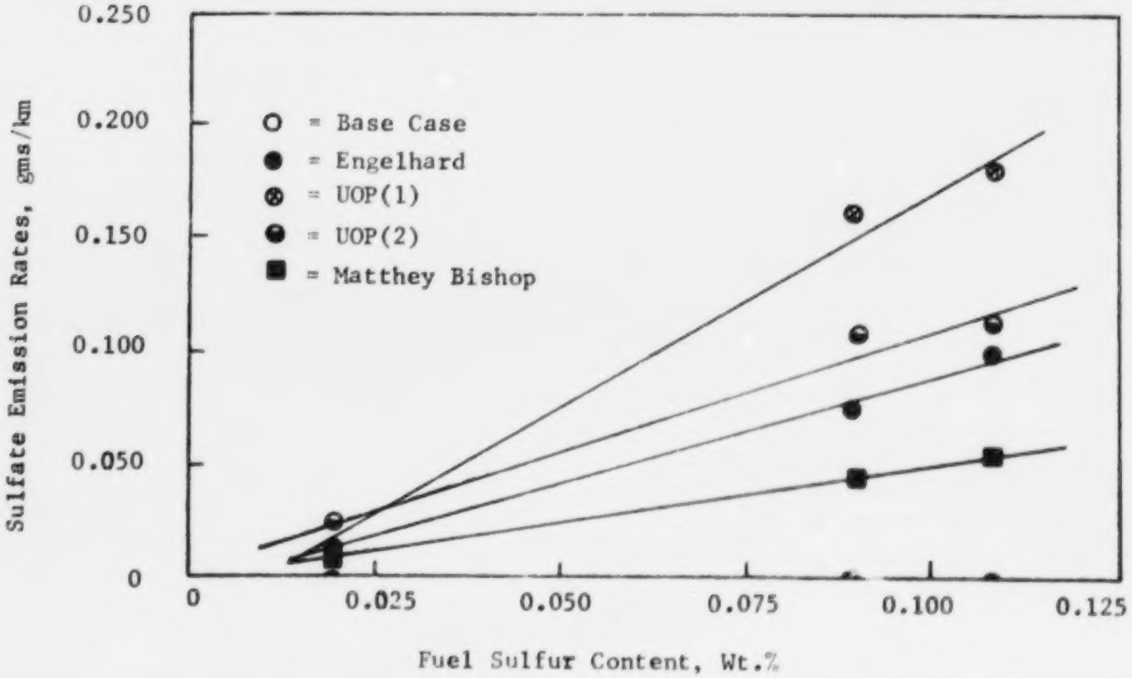


FIGURE IV-13

DEPENDENCE OF SULFATE EMISSION RATES, gms/km ON FUEL SULFUR CONTENT PELLETIZED CATALYST EQUIPPED VEHICLE 64 km/hr (40 mph Cruise)

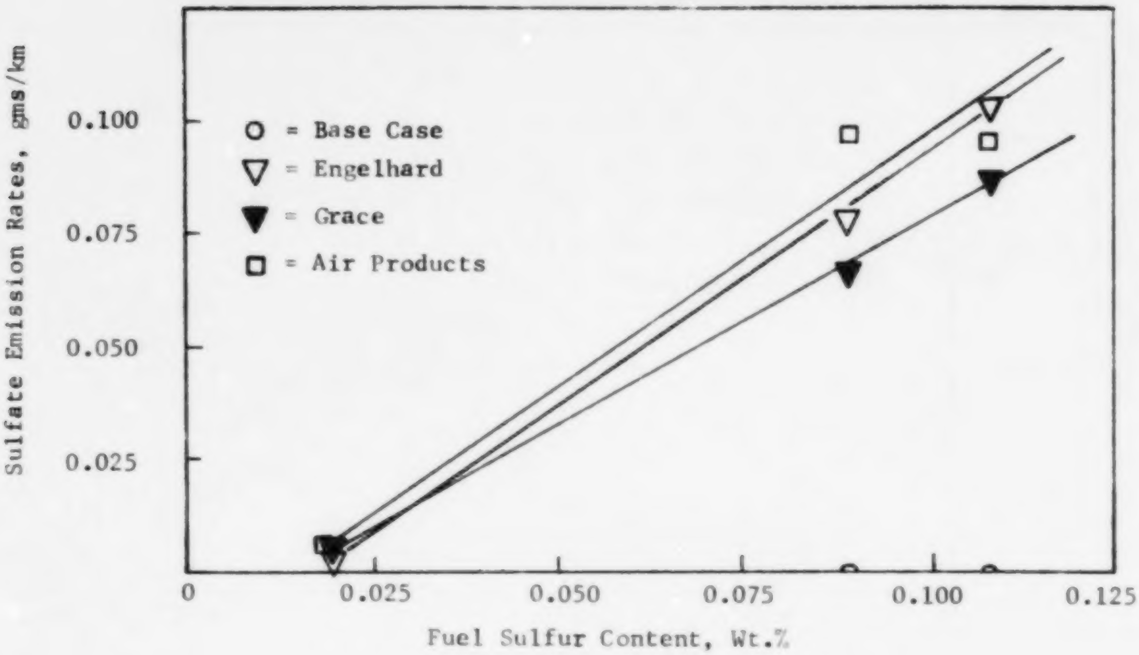
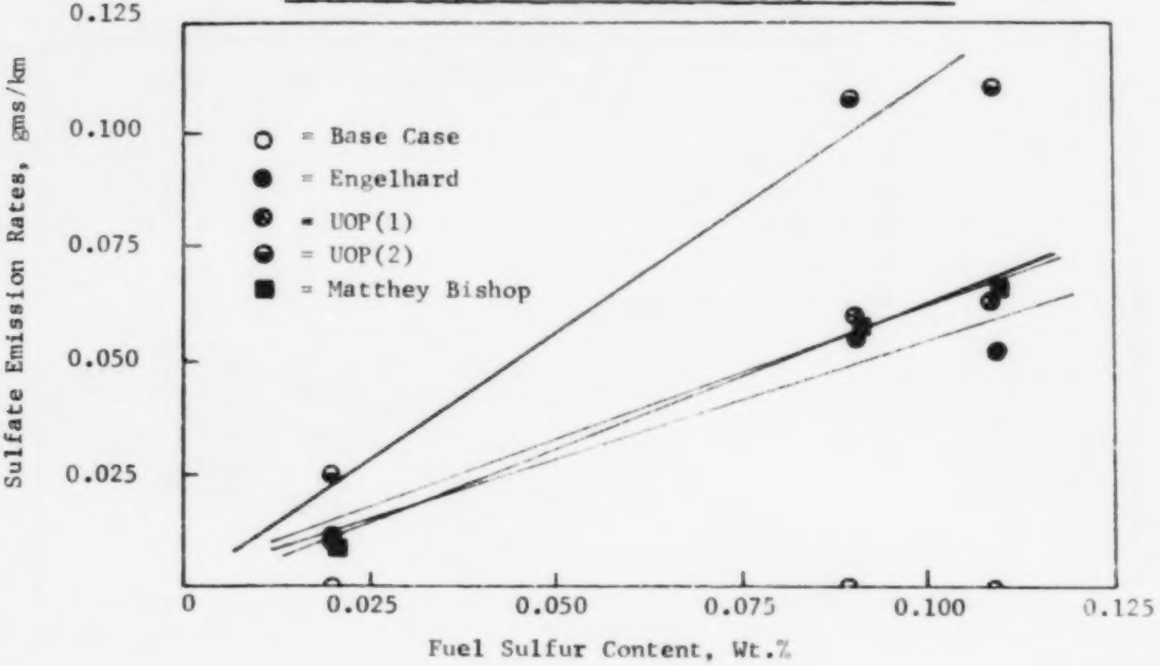


FIGURE IV-14

SULFATE EMISSION RATES VS. FUEL SULFUR CONTENT BASE CASE AND MONOLITHIC OXIDATION CATALYSTS (96 or 113 km/hr Cruises)



At the higher cruise speeds 96 or 113 km/hr (60 or 70 mph), the sulfate emissions from the monolithic oxidation catalyst equipped vehicles were essentially linear with fuel sulfur content. These results are shown in Figure IV-14. The second UOP system emitted higher levels of sulfates than did the first one, the reverse of the emission rates at the lower cruise speeds. One possible reason for this type of reversal in relative emission rates is that the vehicle speed when the second UOP catalyst was tested was 96 km/hr as opposed to 113 km/hr for the first system. Again, the sulfate emission rates with the base case vehicle are too low to be sensibly plotted on the figures below.

Basically similar results were obtained with the pelletized oxidation catalysts, Figure IV-15. The results are shown as straight lines although there are apparent departures from linearity. At the high speed cruises, the sulfate emission rates observed with these catalysts are comparable to those observed with monolithic catalysts. This indicates that sulfate storage on the pelletized catalyst system is not a major factor during high speed cruise. Consequently, under these conditions, both types of catalysts exhibit equivalent sulfate emission rates.

The total particulate emission rate when the vehicle was equipped with NO_x reduction catalysts did not depend on the fuel sulfur content on the 1975 FTP. In fact, as was previously shown in Figure IV-3, the total particulate emission rates obtained with these catalysts on the 1975 FTP was indistinguishable from the base case vehicle emission rates. This was the case because under FTP conditions, the levels of sulfate emitted were comparable to that emitted by the unequipped test vehicle, Table IV-1.

Table IV-1

Average Sulfate Emission Rates (Initial and Final 1975 FTP) from NO_x Reduction Catalyst Equipped Vehicle, and Base Case Vehicle

NO_x Reduction Catalyst	Fuel Sulfur Wt.%	Sulfate Emission Rate, gms/km
None	0.019	0.002
None	0.091	0.002
None	0.110	0.002
Grace	0.019	0.002
Grace	0.091	<0.001
Grace	0.110	0.004
Gould	0.019	0.001
Gould	0.091	<0.001
Gould	0.110	<0.002

On the steady state cruises however, the total particulate emission rates with the NO_x reduction catalyst equipped test car were linearly dependent on fuel sulfur content as previously depicted in Figures IV-6 and IV-9. This dependence on fuel sulfur content was due to production of sulfate under the lean operating conditions of the cruise test runs. Figures IV-16 and IV-17 show the sulfate emission rates with both NO_x reduction catalysts as a function of fuel sulfur content.

FIGURE IV-15

SULFATE EMISSION RATES VS. FUEL SULFUR CONTENT
BASE CASE AND PELLETIZED OXIDATION CATALYSTS
(96 or 113 km/hr Cruises)

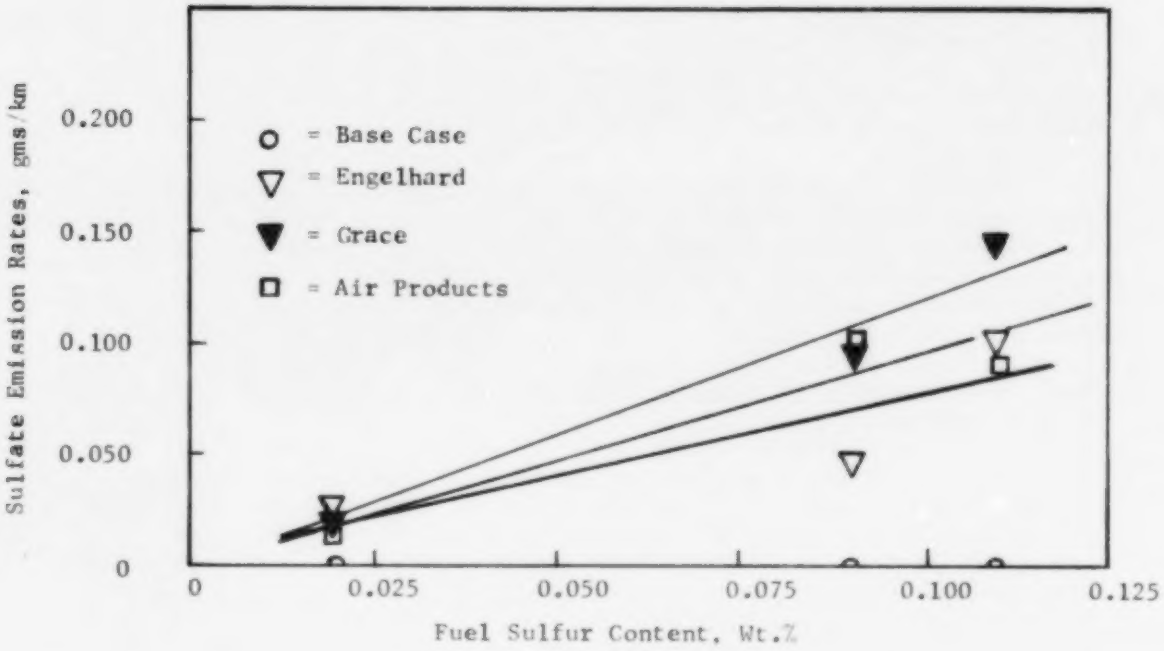


FIGURE IV-16

DEPENDENCE OF SULFATE EMISSION RATES, gms/km ON FUEL
SULFUR CONTENT, VEHICLE EQUIPPED WITH NO_x REDUCTION CATALYSTS
64 km/hr (40 mph) Cruise

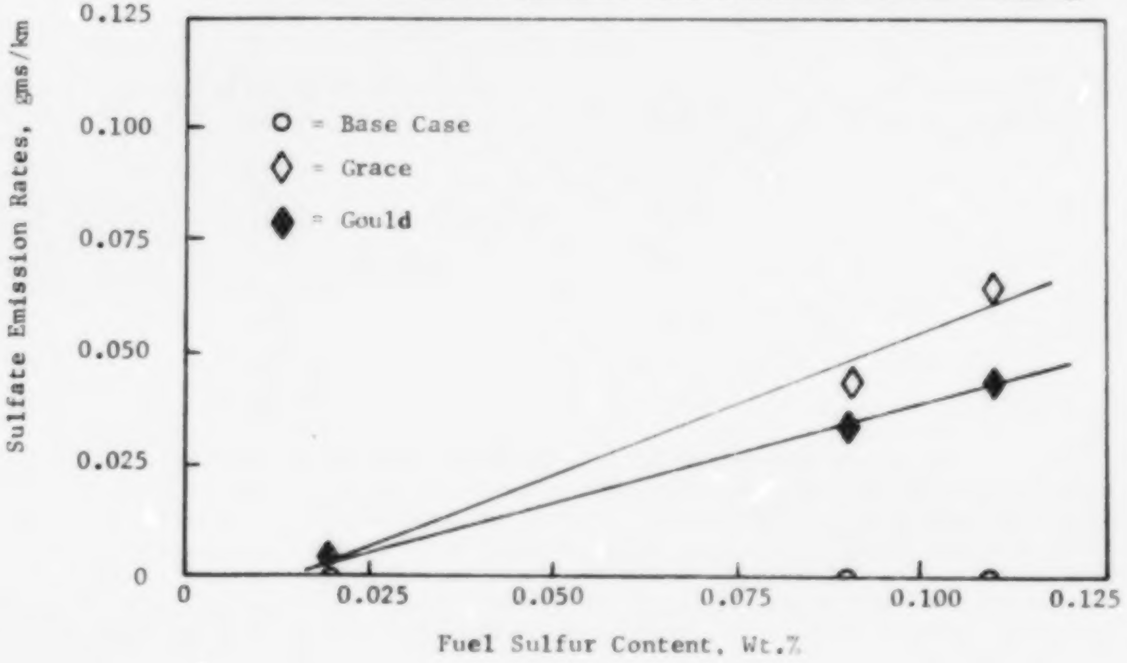
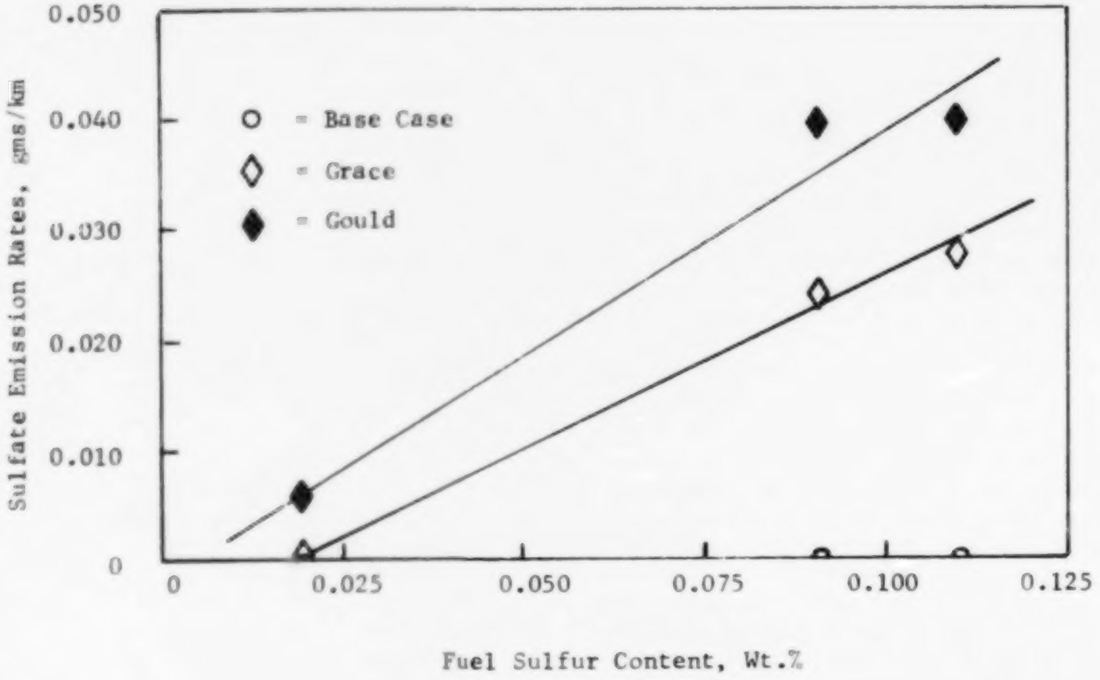


FIGURE IV-17

DEPENDENCE OF SULFATE EMISSION RATES, gms/km
ON FUEL SULFUR CONTENT, VEHICLE EQUIPPED WITH NO_x REDUCTION CATALYSTS
96 km/hr (60 mph) Cruise



Subsequent air/fuel ratio measurements showed that even with the Exhaust Gas Recycle system removed, the vehicle operated much of the time at near stoichiometric and net lean conditions. It is assumed that the emitted sulfate was catalytically produced under lean operating conditions during the cruise test modes. Although the vehicle went net lean during the acceleration portions of the FTP, the duration of the lean operating regime is apparently too transient to produce significant quantities of sulfates.

IV.1.4 Exhaust Sulfur Material Balance

The predominant sulfur compounds in vehicular exhaust are SO2 and sulfate particulate. Consequently, the fate of fuel sulfur could be adequately determined by an accounting of these two exhaust components. Figures IV-18 to IV-26 show the SO2 and sulfate measurements for all catalyst/fuel combinations in terms of the fraction of gasoline sulfur accounted for by the sum of SO2 and sulfate. The detailed data are presented in Appendix E.

Figure IV-18 shows the SO2 and sulfate emissions for the monolithic catalysts for FTP conditions, Figure IV-19 for the 64 km/hr cruise; and Figure IV-20 for the 96 and/or 113 km/hr cruise. Figure IV-21 shows the SO_2 and sulfate emissions for the pelletized catalysts for FTP conditions, Figure IV-22 for the 64 km/hr cruise; and Figure IV-23 for the 96 and/or 113 km/hr cruise. Figure IV-24 shows the SO2 and sulfate emissions for the NO_x reduction catalysts for FTP conditions, Figure IV-25 for the 64 km/hr cruise; and Figure IV-26 for the 96 km/hr cruise.

IV.1.4.1 Sulfur Material Balance With Monolithic Catalysts

Figure IV-18 shows the average total sulfur emissions for the four monolithic catalysts under 1975 FTP conditions. The shaded bars represent the percentage of the total sulfur consumed in the engine emitted as sulfate, the clear bars the percent of fuel sulfur emitted as SO_2. With the exception of the Matthey Bishop monolith system, the exhaust sulfur material balance is poor. Much of the fuel sulfur cannot be accounted for in exhaust either as gaseous or particulate components.

The lack of a sulfur material balance is attributed to sulfate storage on the catalyst-substrate system. When conversions of exhaust SO_2 is low, adequate sulfur material balances can be obtained. For example, earlier work on conventional vehicles in which conversions to sulfate were less than one percent showed that the fuel sulfur could be quantitatively accounted for predominantly as SO_2(18). It may be inferred therefore that the Matthey Bishop oxidation catalyst is less active for SO_2 conversion than the other monoliths based on the higher SO_2 emission rates observed with that system which was almost

FIGURE IV-18

SO_2 AND SULFATE EMISSIONS FOR MONOLITHIC CATALYSTS FOR THE 1975 FTP

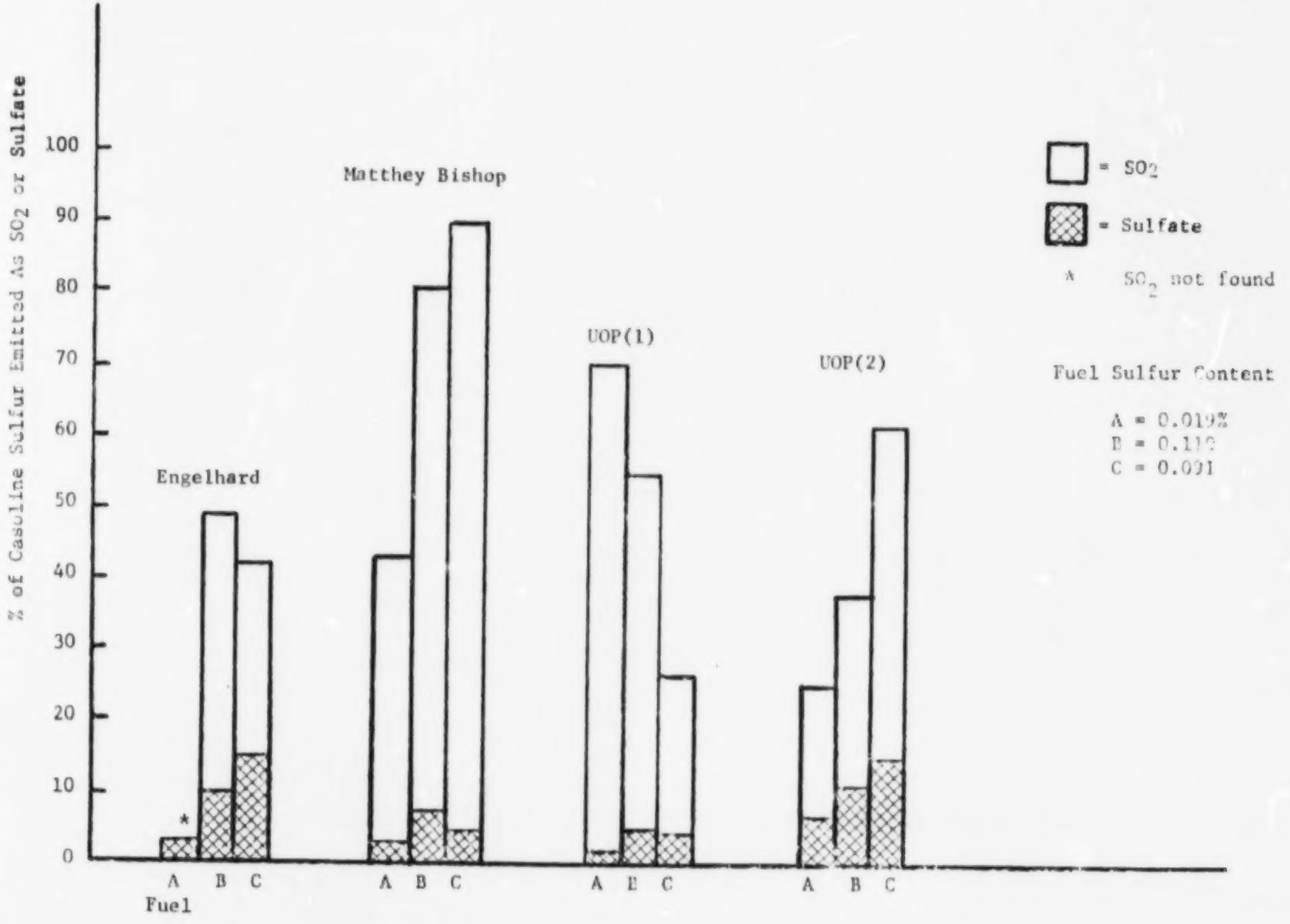


FIGURE IV-19

SO_2 AND SULFATE EMISSIONS FOR MONOLITHIC CATALYSTS AT 64 gm/km CRUISE

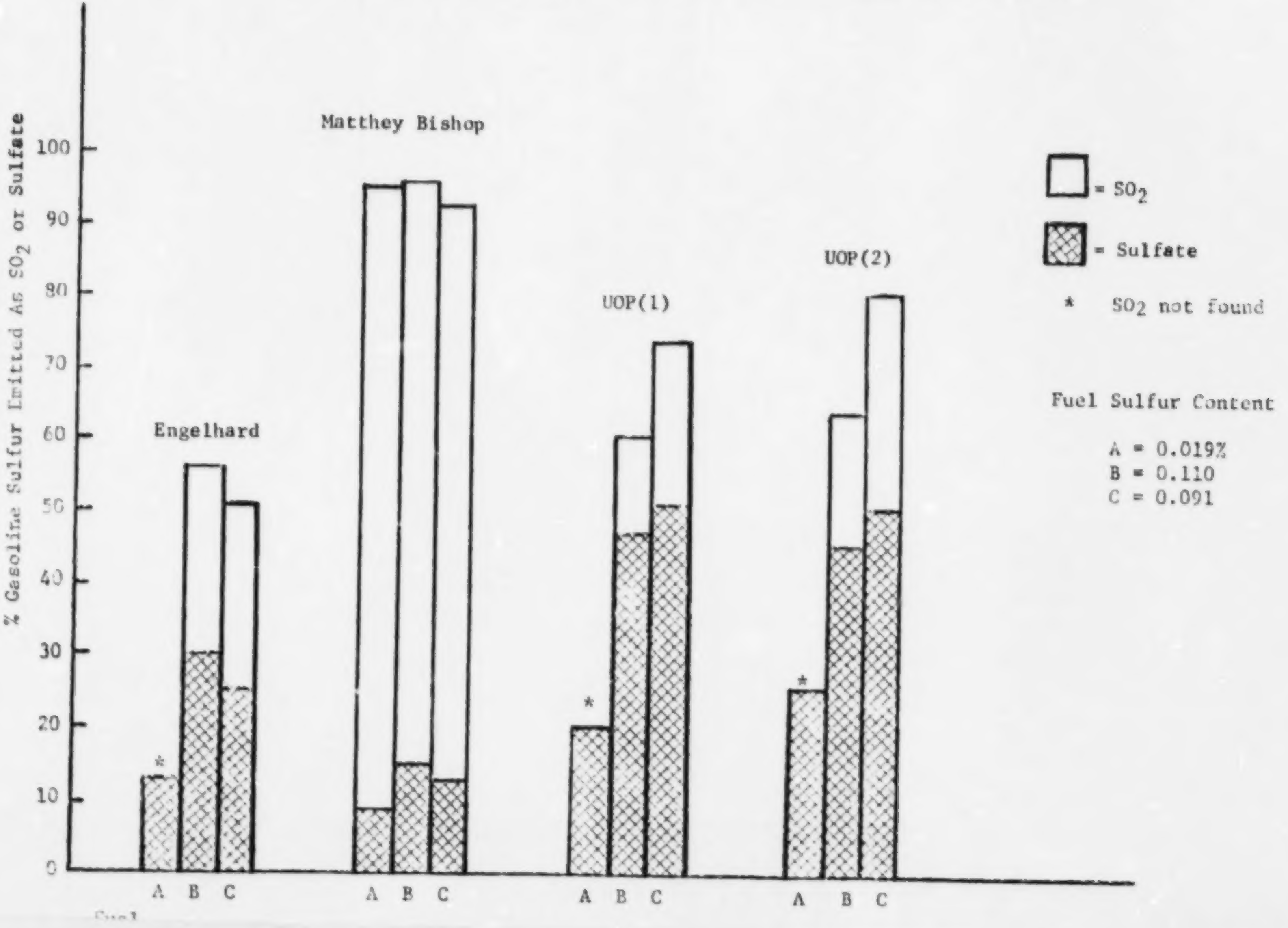


FIGURE IV-20

SO_2 AND SULFATE EMISSIONS FOR MONOLITHIC CATALYSTS AT 96-113 km/hr CRUISE

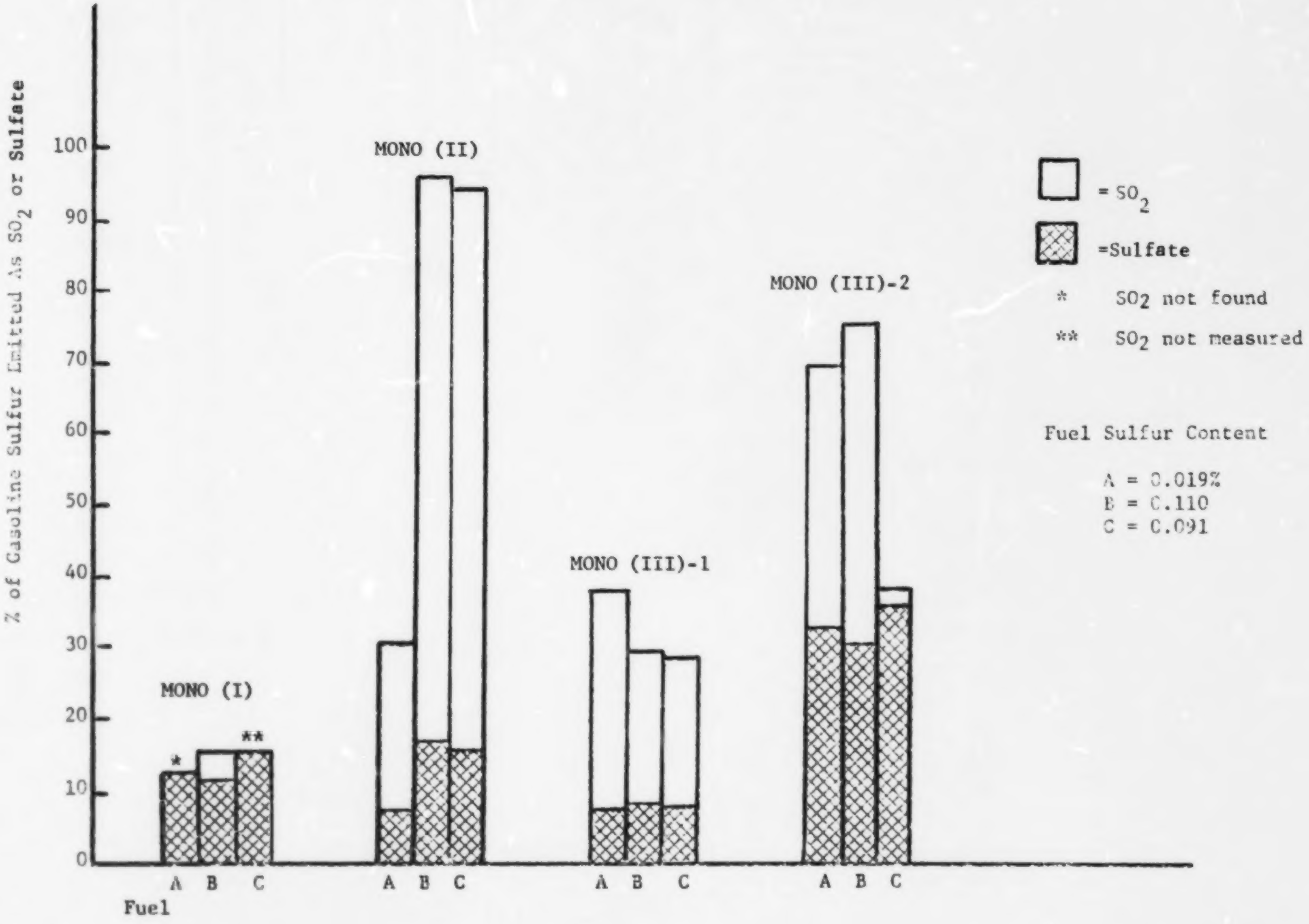


FIGURE IV-21

SO_2 AND SULFATE EMISSIONS FOR PELLETED CATALYSTS FOR THE 1975 FTP

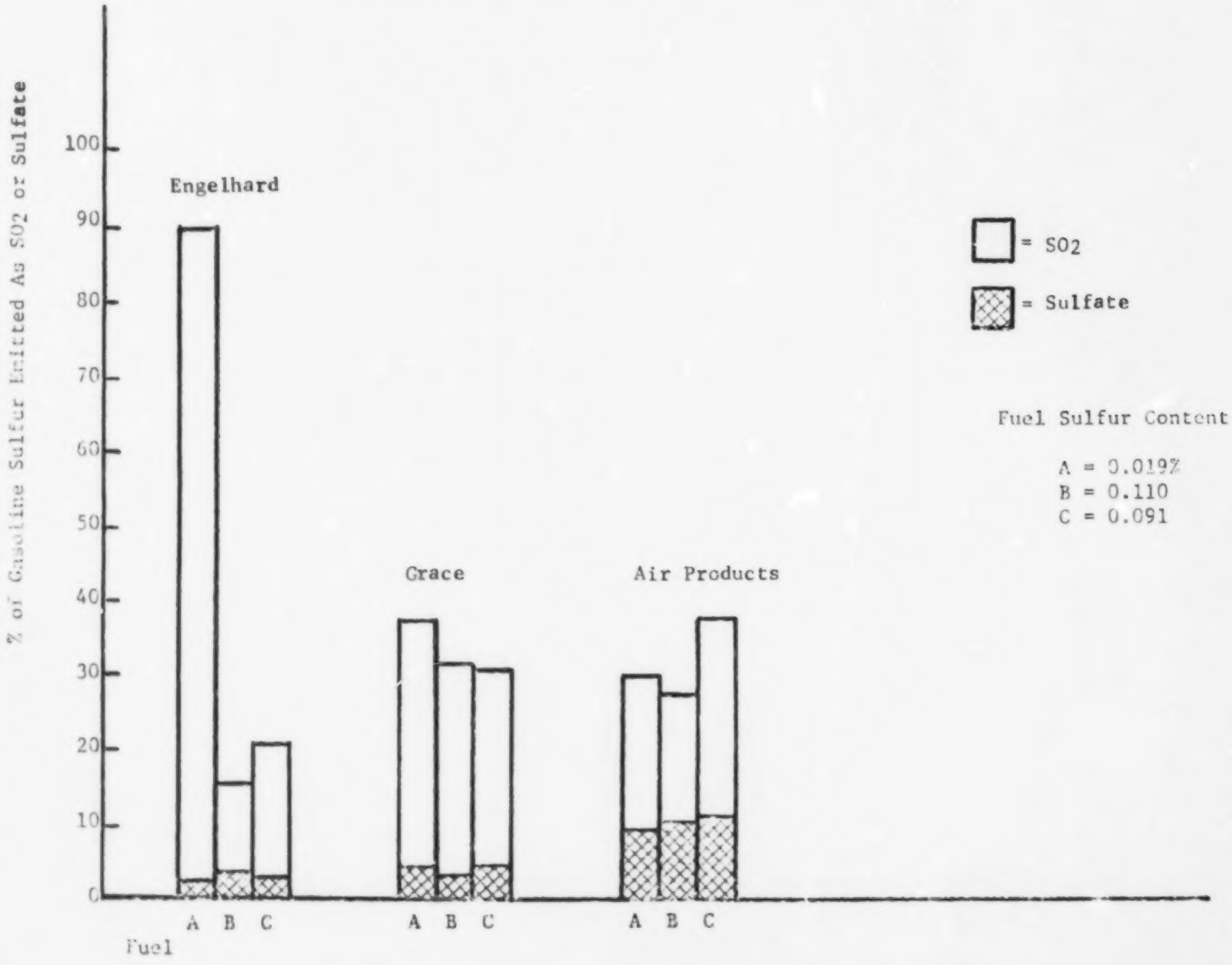


FIGURE IV-22

SO_2 AND SULFATE EMISSIONS FOR PELLETED CATALYSTS AT 64 km/hr CRUISE

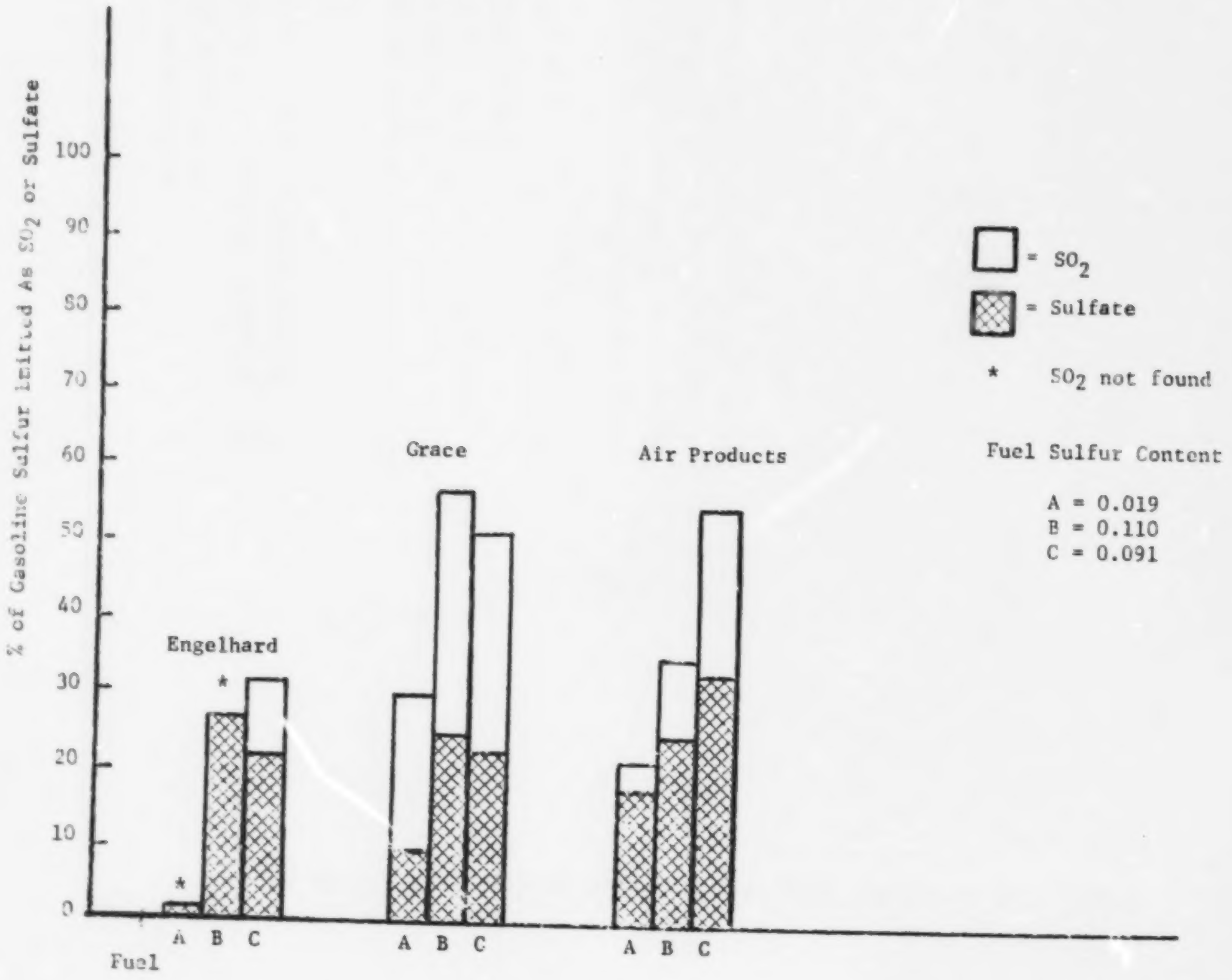


FIGURE IV-23

SO_2 AND SULFATE EMISSIONS FOR PELLETED CATALYSTS AT 96-113 km/hr CRUISE

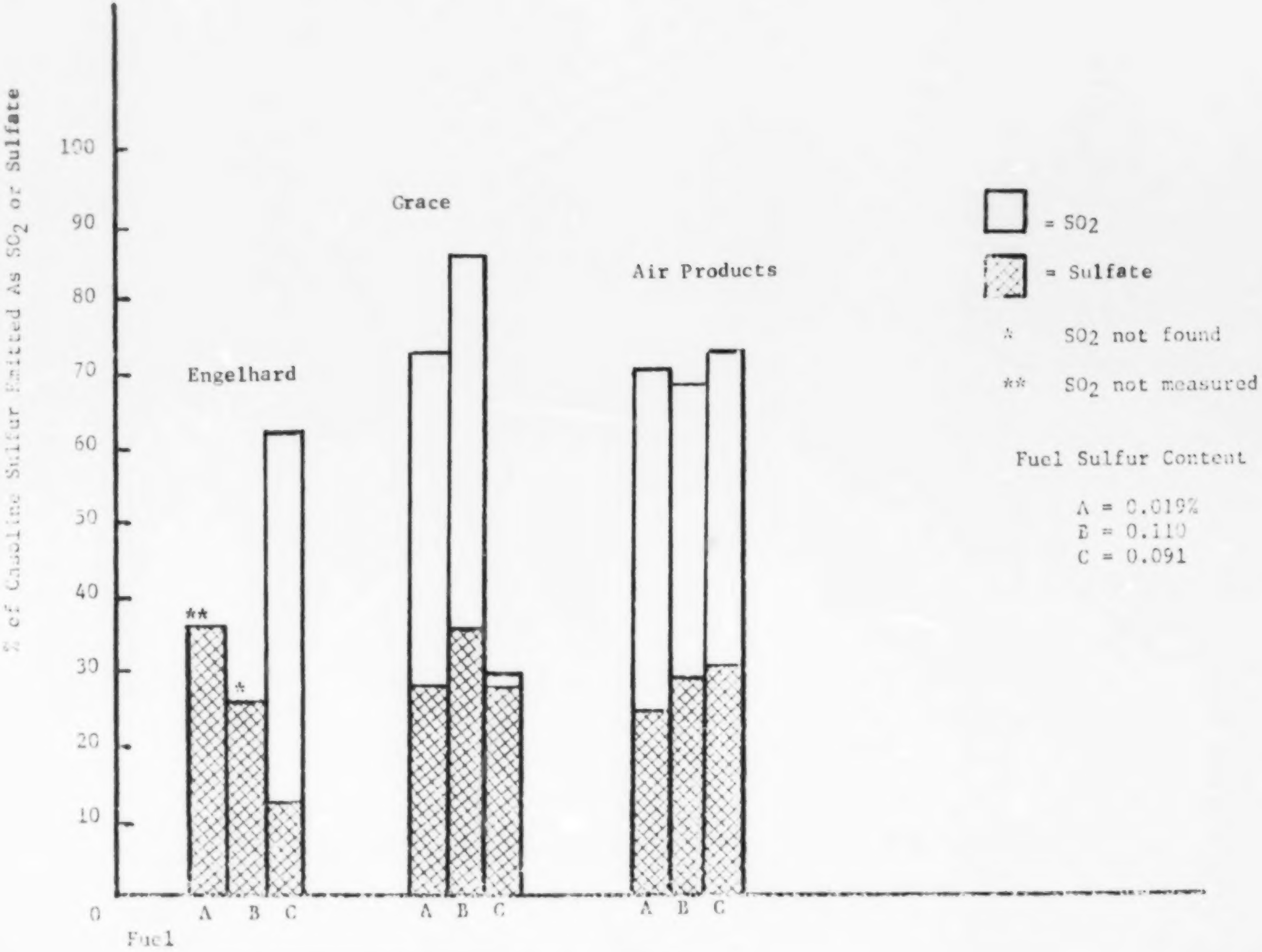


FIGURE IV-24

SO_2 AND SULFATE EMISSIONS FOR NO_x REDUCTION CATALYSTS FOR THE 1975 FTP

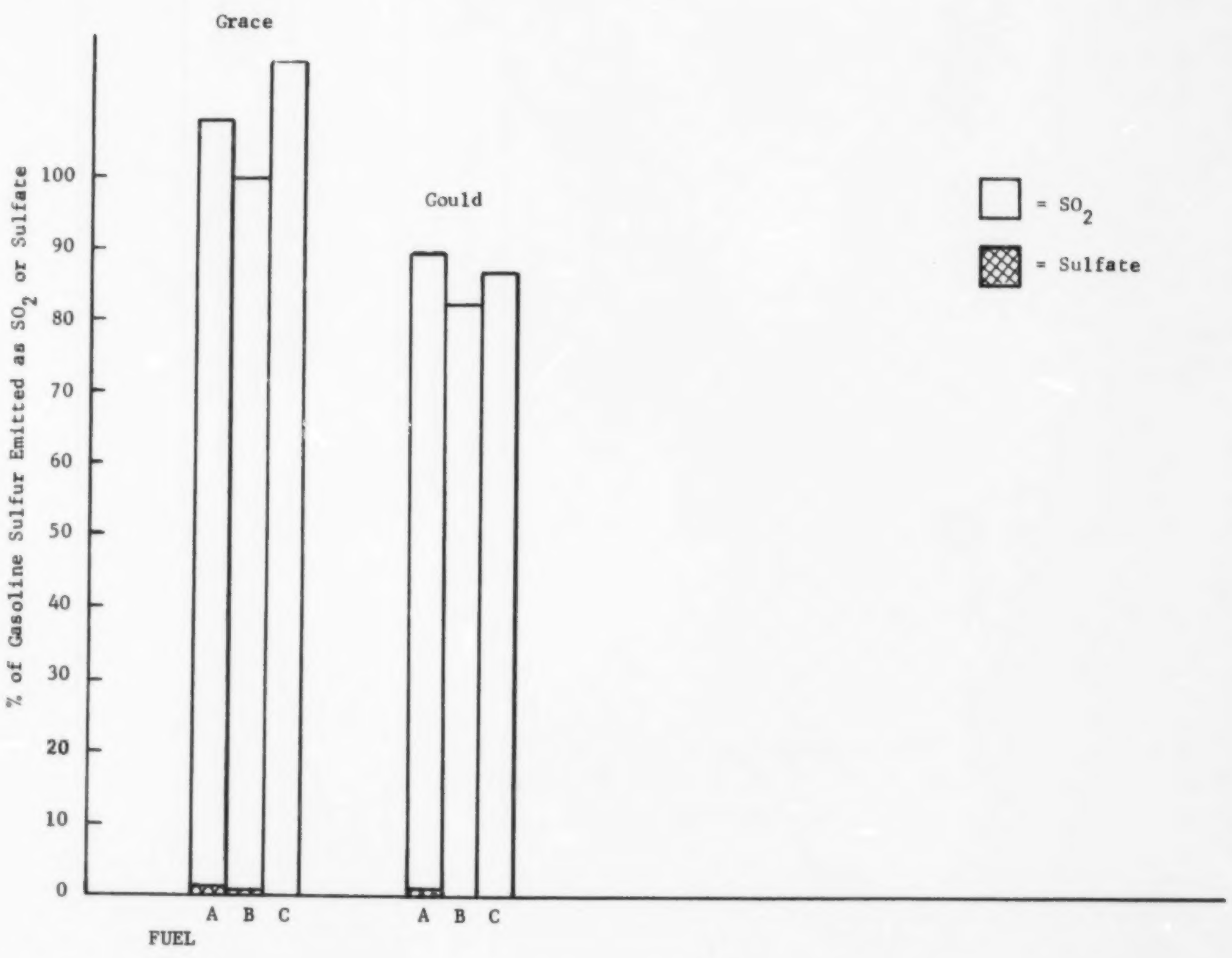


FIGURE IV-25

SO_2 AND SULFATE EMISSIONS FOR NO_x REDUCTION CATALYSTS AT 64 km/hr CRUISE

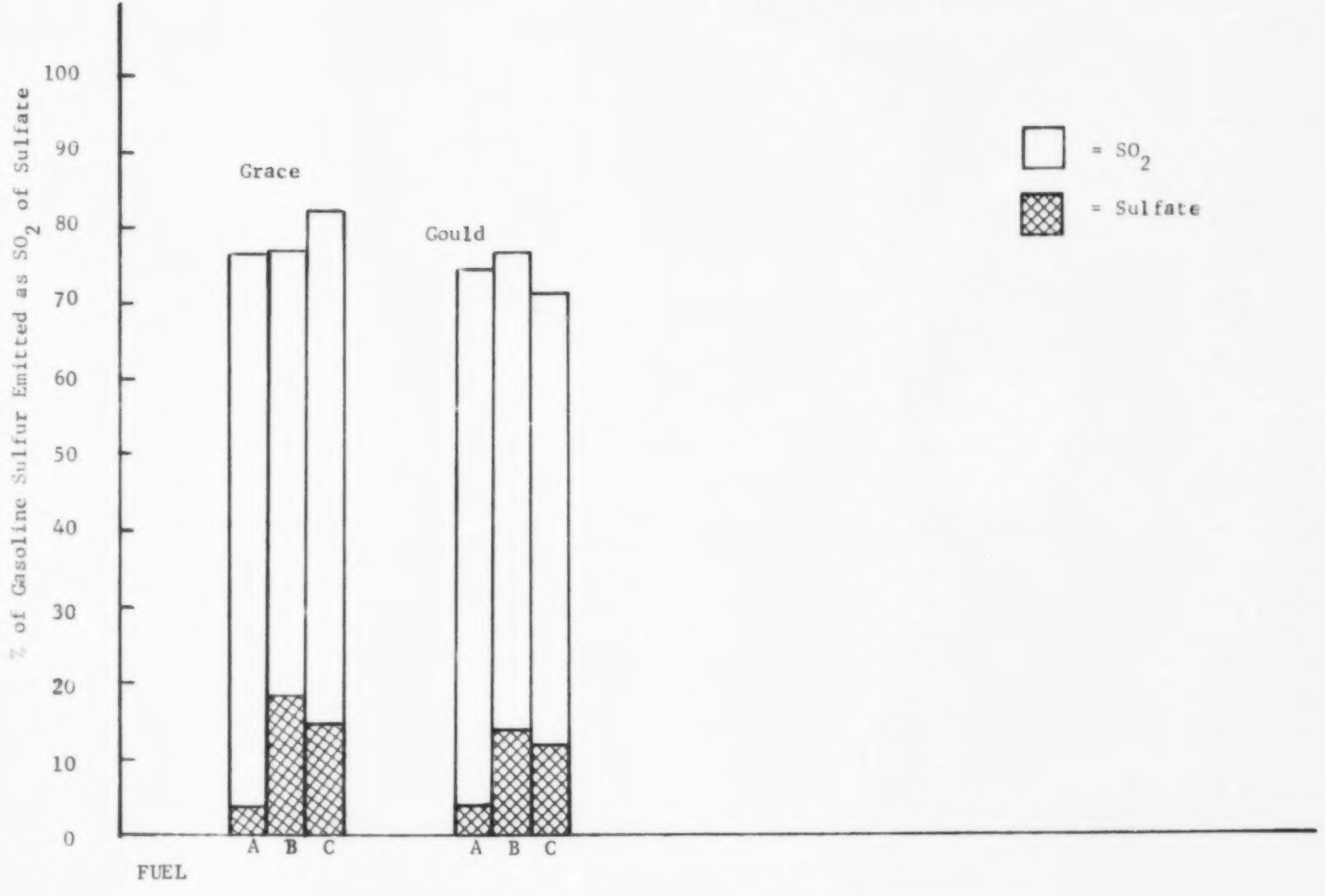
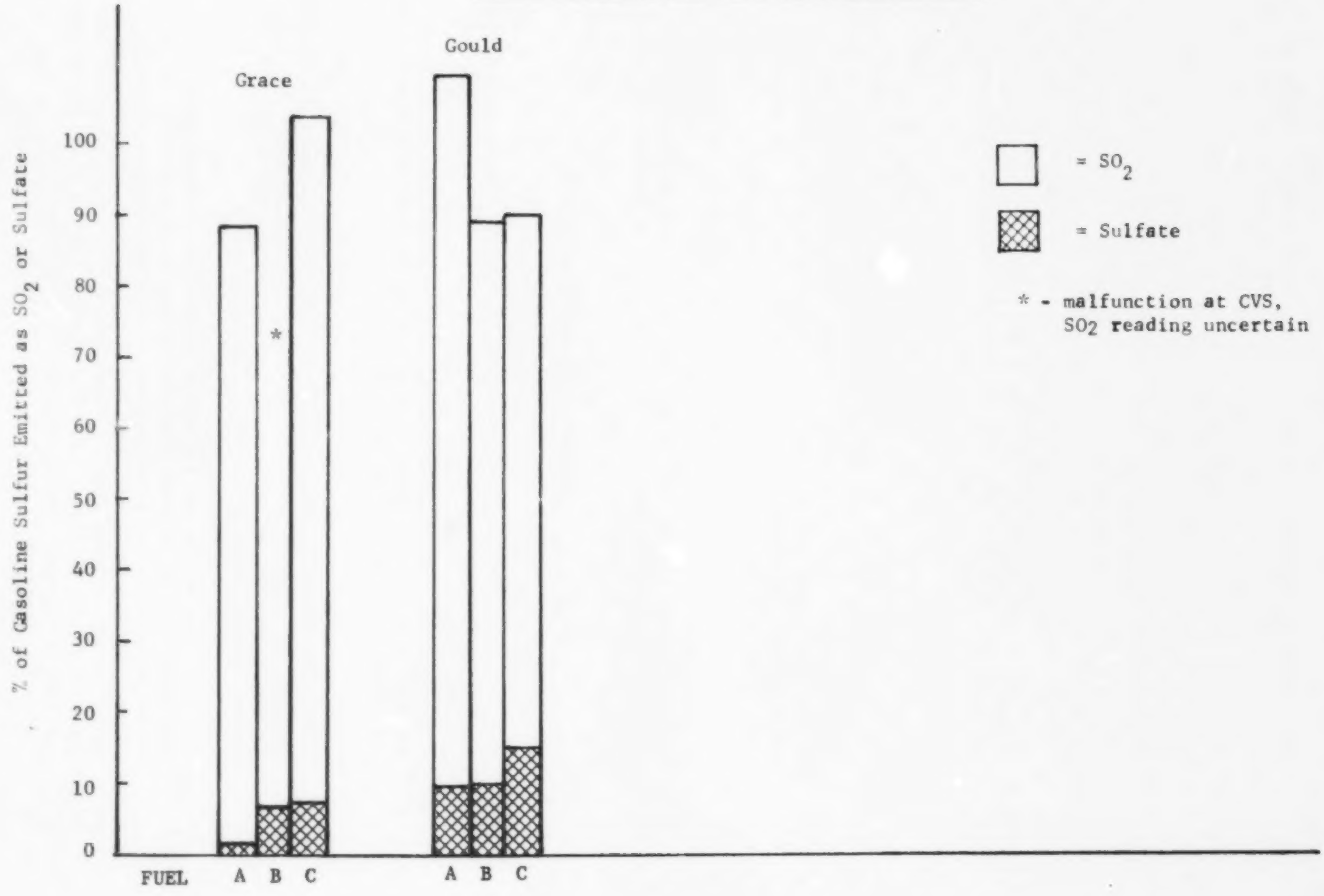


FIGURE IV-26

SO_2 AND SULFATE EMISSIONS FOR NO_x REDUCTION CATALYSTS AT 96 km/hr CRUISE



sufficient in itself to account for the fuel sulfur. Although the emitted sulfate levels obtained on the FTP with the UOP(1) catalyst system were comparable to that obtained with the Matthey Bishop catalyst, the SO_2 emission rates were considerably lower. This indicates that the extent of conversion of SO_2 to sulfate is greater with the UOP(1) catalyst but that an appreciable portion of the sulfate made does not show up in the emitted exhaust.

This is substantiated by the similar behavior on the 64 km/hr (40 mph) cruises. Again, the total sulfur balance for the Matthey Bishop catalyst is nearly 100%, while the other monolithic catalysts on the average account for 55 to 75% of the fuel sulfur consumed. The sulfate yields from the Matthey Bishop catalyst are considerably lower (~15%) than the other monoliths which averaged about 36% and ranged from 12 to 53%.

On the high speed cruises (96-113 km/hr), the sulfate emission rates with the Matthey Bishop system were comparable to that of the Engelhard and UOP(1) monoliths. However, the SO_2 emission rates with the Matthey Bishop system were higher than that observed with the other catalysts and again, a better sulfur material balance was obtained. These results indicate that although the sulfate emission rates of the catalyst systems discussed above are comparable, the actual SO_2 conversions may be considerably different.

Although the two UOP catalysts exhibited similar behavior on the lower cruise speed test mode (in terms of SO_2 and sulfate emissions), at the higher cruise speeds, the UOP(2) system exhibited essentially the same SO_2 emission rates, but higher sulfate emission rates than the UOP(1) monolith.

IV.1.4.2 Sulfur Material Balance With Pelletized Catalysts

As shown in Figures IV-21 to IV-23 still greater deficiencies in sulfur balances are obtained with pelletized catalyst systems. On the FTP, Figure IV-21, only 20-35% of the total fuel sulfur is accounted for, the Engelhard and Grace catalysts emitting about 4% of the fuel sulfur as sulfate, the Air Products System emitting about 10% of the fuel sulfur as sulfate.

Similar behavior is exhibited on the 64 km/hr (40 mph) cruises. The sulfur material balance deficiencies obtained with the pelletized systems are greater than that obtained on their monolithic counterparts. Thirty to 60% of the fuel sulfur was accounted for, with the sulfate yields ranging from 20 to 30%.

On the 96 or 113 km/hr cruises the sulfur material balance was generally better than what was obtained on the 1975 FTP's or the 64 km/hr cruises. Sulfate conversions averaged from about 25 to 30%. The sulfur dioxide accounted from about 39 to 51% of the fuel sulfur, which is higher than what was obtained on these systems, on either the FTP or 64 km/hr cruises. The percent of the fuel sulfur accounted for (SO_2 + sulfate) ranged from 63 to 80%.

The higher SO_2 emission rates on the high speed cruises, indicative of lower SO_2 conversions may be due to the following factors:

(1) The higher space velocities at the high speed cruises could result in lower conversions. Bench scale studies(19) assessing the effect of space velocity on conversion substantiate this claim.

(2) Because of the unfavorable equilibrium ($SO_2 + 1/2\ O_2 \rightleftharpoons SO_3$), conversion is less favorable at the higher catalyst temperatures which would prevail at the high speed cruises.

The sulfur material balance would be expected to be better because, in addition to the above, because of the reduced tendency to store sulfur at the higher cruise speeds (and consequently) higher catalyst temperatures. Sulfate storage experiments carried out on this contract program are discussed in Section IV.1.5.

IV.1.4.3 Sulfur Material Balance With NO_x Reduction Catalysts

Figure IV-24 shows the average total sulfur emissions for the two NO_x reduction catalysts under 1975 FTP conditions. Average total sulfur recoveries for both systems was about 97%. Sulfate emissions amounted to less than 1% conversion. Under FTP conditions, the sulfur material balance with these catalysts was similar to that obtained with the unequipped vehicle.

Sulfate emissions increased for both catalyst systems on both cruise test modes, Figures IV-25 and 26. Conversions based on emitted sulfates ranged from 4 to 18% on the 64 km/hr cruise. The percent of total fuel sulfur accounted for in this cruise mode ranged from 72 to about 82%, higher than that obtained with the vehicle equipped with the oxidation catalysts. The inability to achieve a complete sulfur balance apart from experimental error may be due to some sulfate storage occurring on the NO_x reduction catalyst system.

On the 96 km/hr cruise, the average of the total fuel sulfur accounted for with both systems was 96%. The sulfate emission rates were generally lower than those measured at lower cruise speeds. Sulfate conversions ranged from 1.5 to 15%, averaging about 8 to 9% for both catalysts over all fuel combinations. The SO_2 emission rates were higher on the higher speed cruise mode.

At the two cruise modes both NO_x reduction catalysts resembled the oxidation catalysts in that sulfate particulate was emitted, the emission rate varying in an approximately linear fashion with fuel sulfur content (Section IV.1.3). In addition, the lower conversions at the higher speeds is probably due to the same factors operating to reduce conversion over the oxidation catalysts, namely the higher catalyst temperature and space velocity.

The resemblance to oxidation catalysts is due to the fact that the vehicle in the cruise modes was operating at stoichiometric and net lean conditions. The Gould catalyst contains a small oxidation catalyst ahead of the Ni-Cu reduction catalyst in order to extend its life(20). This oxidation catalyst acts as an exhaust oxygen scavenger. Under stoichiometric or lean conditions this catalyst would also be expected to catalyze the oxidation of exhaust SO_2 to sulfate. Similar considerations apply to the Grace NO_x reduction catalyst, which contains noble metal and therefore could function as an oxidation catalyst for SO_2 under near stoichiometric and net lean conditions (21).

IV.1.5 Sulfate Storage on a Pelletized Catalyst System

Previous studies(3,19) had shown that sulfate can be stored at under cyclic driving conditions and released under high speed cruise conditions. To more fully examine sulfate storage the following experiment was carried out. The test vehicle was reequipped with the Engelhard pelletized catalyst that had been previously tested. The catalyst equipped vehicle was conditioned for 3218 km (2,000 miles) on the 0.091 wt.% sulfur fuel using the Federal Durability Cycle. Following conditioning, the vehicle was cold soaked for 24 hours, and then run through the program test sequence used for screening the catalysts namely 1975 FTP, one hour idle, 64 km/hr one-hour cruise, 96 km/hr two-hour cruise, an overnight soak, and a final 1975 FTP. Unlike the screening study in which the conditioning and test fuel was of the same sulfur content, the test fuel in this case was the 0.019 wt.% sulfur fuel. Conditioning and testing as outlined above makes it possible to determine whether stored sulfate can be released under other than high speed cruise conditions.

The CO, hydrocarbon, NO_x, SO_2, total particulate, sulfate and metal emission rates were determined as in the previous screening studies. Table IV-2 below shows that the hydrocarbon and NO_x emissions are similar in both types of runs (standard vs storage), but that large differences in CO emissions are obtained.

Table IV-2

Comparison of Gaseous Emission Rates of
Vehicle Equipped with Engelhard Pelletized
Oxidation Catalyst Operated on 0.019 Wt % S Fuel

Emission Rate, gms/km
on 1975 FTP (Initial and Final)

Standard Conditioning			Storage Conditioning		
CO	HC	NO_x	CO	HC	NO_x
2.53	0.22	1.37	1.23	0.19	1.20
2.50	0.22	1.32	1.01	0.19	1.09

The decrease in CO emissions was unexpected and cannot be satisfactorily explained at present. Although reduction of stored sulfate by CO can occur, the increase in SO_2 emissions that was observed was not sufficient to account for the decrease in CO emissions. The increased SO_2 emissions after storage conditioning will be considered shortly.

As shown below in Table IV-3, larger differences were observed with respect to SO_2, sulfates, and total particulate.

Table IV-3

Emission Rate of Indicated Exhaust
Component, gms/km for Test Runs Following
Standard Conditioning (A), and Storage Conditioning (B)

Test Type	SO_2		H_2SO_4		Total Particulate	
	A	B	A	B	A	B
75 FTP	0.015	0.050	0.003	0.044	0.061	0.105
64 km/hr	0.0	0.016	0.001	0.119	0.009	0.258
96 km/hr	---	0.088	0.027	0.103	0.115	0.239
75 FTP	0.017	0.077	0.002	0.100	0.036	0.152

The large increase in total particulate emission rates is due to increased sulfate emissions as a result of release of stored sulfate, as shown in Tables IV-4 and IV-5 below.

Table IV-4

Storage Experiments, Pelletized
Engelhard Catalyst, 0.019 Wt % S Test Fuel

	% Fuel Sulfur Accounted For		
Test	As Sulfate	As SO_2	Total
75 FTP	50	83	133
64 km/hr	191	38	229
96 km/hr	157	200	357
75 FTP	105	126	231

Table IV-5

Standard Screening Tests, Pelletized Engelhard Catalyst, 0.019 wt.% Test Fuel

	% Fuel Sulfur Accounted For		
Test	As Sulfate	As SO_2	Total
75 FTP	3.2	24.2	27.4
64 km/hr	1.5	0.0	1.5
96 km/hr	24.6	35.5	60.1
75 FTP	2.1	53.3	55.4

The 64 km/hr cruise results are reminiscent of earlier storage studies(3,19) in that sulfate yields in excess of 100% (based on the sulfur content of the test fuel and fuel economy are obtained). However, these storage tests have also shown that sustained storage of sulfate can result in the following situations:

(1) Sulfate yields exceeding 100% can be obtained on lower cruise speeds such as 64 km/hr.

(2) Sulfate yields exceeding 100% can be obtained under cyclic driving conditions.

(3) The total exhaust sulfur out (SO_2 + sulfate) can exceed 100% although each component may not.

(4) Sulfur dioxide emissions alone can exceed the theoretical fuel consumption values as it did in 96 km/hr cruise and the second 1975 FTP.

Although sulfate yields exceeding theoretical values have been previously observed, that SO_2 emissions could also exceed theoretical fuel consumption values was unexpected. Increased SO_2 emissions could occur through several routes. Reduction of a portion of the stored sulfate could occur by the following reaction:

$$\text{Stored } H_2SO_4 + CO \longrightarrow SO_2 + H_2O + CO_2$$

If the test fuel is one of low sulfur content, the fraction of exhaust CO that is oxidized need not be large in order that SO_2 yields exceeding 100% can occur. Under these circumstances, the CO emission rate would be undistinguishable from that obtained in a standard run.

As mentioned previously, the decrease in CO emissions is too great to account for the increased SO_2 emission. A decrease in CO emission rate from 2.5 to 1.0 gms/km by reduction of stored sulfate would result in an increase in SO_2 emissions of 3.4 gms/km. This is far in excess of the total SO_2 emission rates observed even with SO_2 yields as high as 200%.

Another possible mechanism operating to produce greater than 100% yields of SO_2 is the catalytic decomposition of some of the stored sulfate as shown below:

$$\underset{\text{(stored)}}{H_2SO_4} \longrightarrow H_2O + SO_2 + 1/2\ O_2$$

It would not be possible to decide which mechanism or if both were operating to produce SO_2 emissions exceeding theoretical based on how the storage tests were conducted. Separate experiments would be required to determine the mechanism of increased SO_2 production, which were not called for in the contract.

IV.1.6 Bound Water in Exhaust Particulate

Previous work(3) had shown that the water content of exhaust particulate increases with increasing sulfate content, but that the ratio of water to sulfate was relatively constant. Moreover this ratio corresponds approximately to what would be expected from the equilibrium % composition-relative humidity relationship at conditions under which the water analysis took place. This relationship at 20°C is depicted in Figure IV-27.

As shown in Figure II-6 Section II.2.5, the average relative humidity at the filter during cyclic test conditions is about 20% at 90°F. This corresponds to 28% relative humidity at room temperature. The particulate filter is conditioned and weighed in a constant temperature humidity room (about 45% RH).

It can be seen from Figure II-27 that a change from 28% relative humidity to 45% relative humidity results in minor increase in the weight fraction of water. Thus the weight of particulate should when sulfuric acid present correspond closely to the quantity collected on the filter during a run. The relative humidity of the analytical laboratory although not maintained constant, is probably close to that in the weighing room, which means that the quantity of water measured by the Karl Fisher method is a reliable measure of the quantity of bound water collected on the particulate filters during a test run. Table IV-6 below shows the quantities of bound water in terms of emission rates as determined by Karl Fisher titration for the base case vehicle and several catalyst runs on the 1975 FTP.

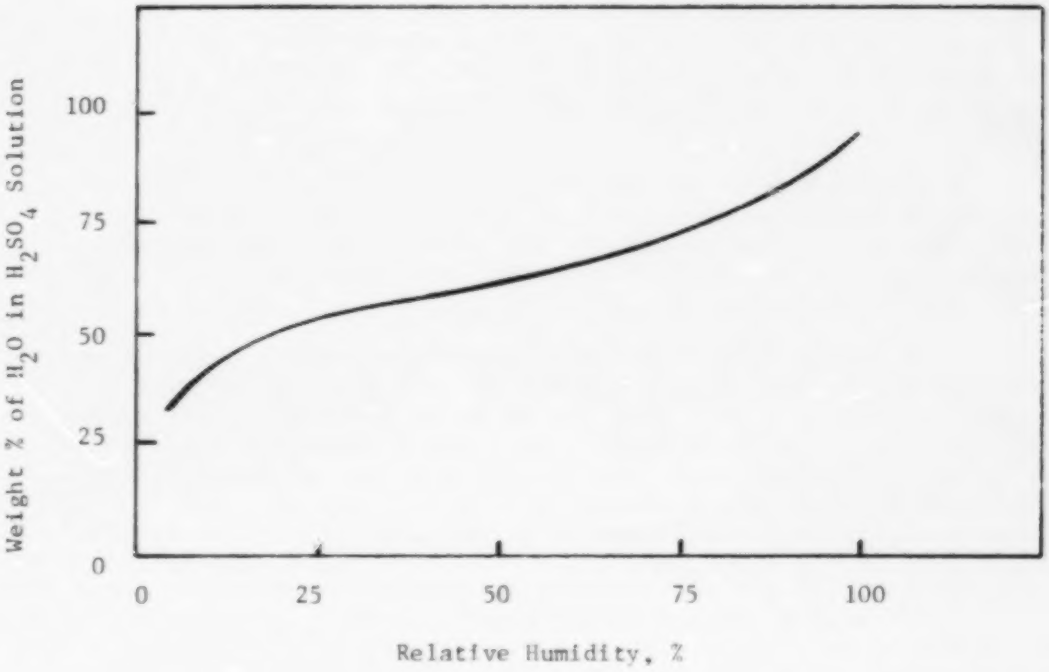
Table IV-6

Relation of Bound Water to Sulfate Emissions

Run No.	% Fuel Sulfur	Catalyst	Emission Rate, gms/km on 1975 FTP Total Particulate	H_2SO_4	H_2O
20	0.019	None	0.019	0.001	<0.001
46	0.091	Engelhard Monolith	0.226	0.087	0.092
61	0.091	Engelhard Pellet	0.062	0.016	0.013
75	0.110	UOP(1)	0.090	0.027	0.022
106	0.091	Grace Reduction	0.019	0.001	<0.001
121	0.091	Gould Reduction	0.031	0.001	<0.001
135	0.110	Grace Pellet	0.065	0.034	0.029
151	0.091	UOP(2)	0.173	0.078	0.085

FIGURE IV-27

EQUILIBRIUM % COMPOSITION - RELATIVE HUMIDITY CURVE FOR AQUEOUS H_2SO_4 AT 20°C



It can be seen that the emission rates of water and H_2SO_4 are comparable and are fairly close to the equilibrium curve shown in Figure IV-27.

Differences from equilibrium could be due to experimental errors in the various analytical determinations. Another reason for the differences is that not all the sulfate (which is what is determined by analysis) is present as the free acid, but as rather a portion may exist as metal sulfates. The latter would be unresponsive to environmental relative humidity conditions. The distribution of sulfate could be ascertained by the difference between sulfate determined by the titrimetric procedure and by titration with base. Although the acid-base titrations were not performed, it may be readily inferred from the close approach to the equilibrium % composition-relative humidity curve that free sulfuric acid is the preponderant sulfate exhaust particulate component. Earlier work(3) has shown that similar considerations would apply to steady state cruises.

IV.1.7 Morphology of Automotive Sulfate Particulate

The morphology of the sulfate deposits on the glass fiber exhaust particulate filters provides direct visual evidence that the free acid is the predominant form of sulfate particulate emitted by oxidation catalyst equipped vehicles. Figure IV-28 shows an electron micrograph of a glass fiber filter from a test with a conventional vehicle in which little sulfate was produced. This filter was used as the last stage of the Andersen Impactor and consequently contains little if any organic particulate matter.

Figure IV-29 is a micrograph of a total filter from a run with an oxidation catalyst equipped vehicle. This filter contained 125 mg of sulfate. The presence of the free acid can be seen by the globular deposits on many of the glass fibers and web-like films that wet many of the fibers. It will be noted that no crystalline particulate matter appears to be collected on the filter indicating that little if any sulfate salts are present. Globular droplets, and wetting of fibers are phenomenon that can only be associated with liquids, providing further evidence that automotive sulfate exists predominantly as the free acid.

It is also of interest to note that the parallel lines running through the micrograph in Figure IV-28 are absent in Figure IV-29. These lines are image distortions due to the presence of static charges. They are absent from the micrograph shown in Figure IV-29 because the sulfuric acid is conductive and can dissipate the static charge. Thus, the process of obtaining an electron micrograph itself provides evidence of the presence of free sulfuric acid.

Figure IV-28

Scanning Electron Micrograph of
Absolute Filter From Andersen Impactor

1,000X 1 MM = 1 MICRON ⊢—⊣ 10 MICRONS

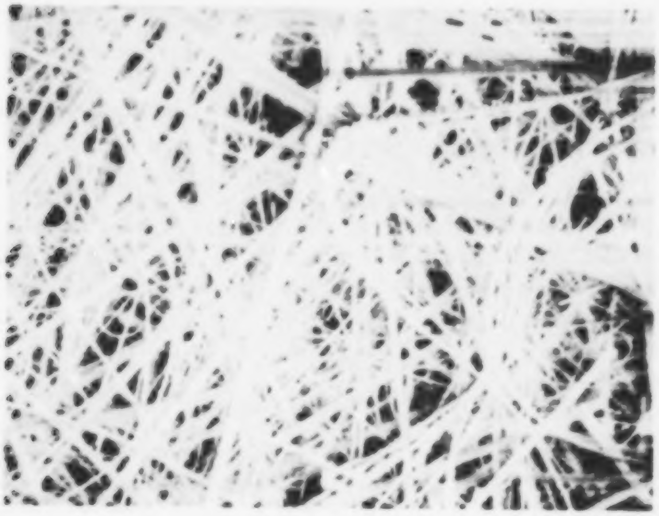
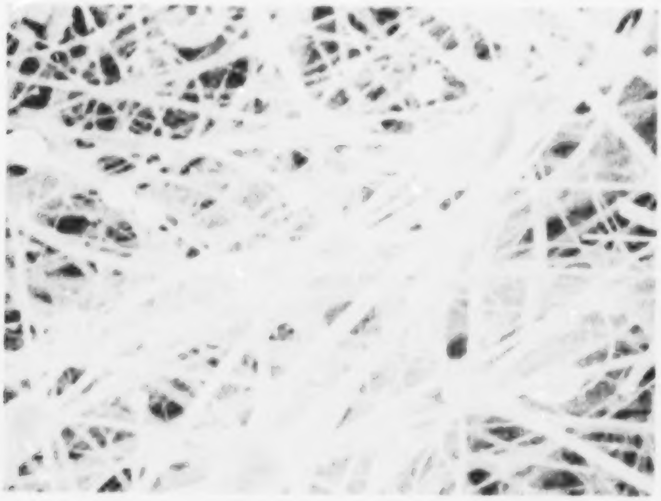


Figure IV-29

Scanning Electron Micrograph of Total
Filter Containing 125 mg of Sulfate

1000X, 1 MM = 1 MICRON ⊢—⊣ = 10 MICRONS



IV.1.8 Non-Sulfate Sulfur Exhaust Particulate

Chemical spot tests were carried out on particulate samples generated from the 1975 FTP and 64 km/hr (40 mph) test runs for non-sulfate sulfur containing particulate matter. The samples analyzed included those from runs on the unequipped vehicle, and when the vehicle was equipped with the various catalysts screened in the test program.

The extreme sensitivity of many of these tests should allow detection of low levels of non-sulfate particulate matter. Negative results establish the maximum emission rate possible based on the sensitivity of the spot test and the mileage accumulated on the particular test run. The spot tests used were those listed in Feigl(22). These are discussed in detail in Appendix A.

The filters were analyzed for the presence of the following sulfur compounds:

thiocarbonyls
thiols
sulfides
disulfides
isothiocyanates
sulfoxides
sulfinic acids
sulfones

The selection of the above compounds as possible exhaust components is based on chemical species known to be present in auto exhaust which could function as precursors to the above compounds or as reactants involved in their production. The basis of this selection is discussed in Appendix D.

All tests for the above compounds were negative. Based on the sample size taken (0.42% of the active filter area), the emission rates of the above compounds cannot exceed the values listed in Table IV-7 below.

Table IV-7

ESTIMATED MAXIMUM EMISSION RATES OF NON-SULFATE SULFUR EXHAUST PARTICULATE

	gms/km	
Compound Type	1975 FTP	64 km/hr cruise
Thiocarbonyl	8×10^{-4}	2×10^{-4}
Thiols	"	"
Sulfides	"	"
Disulfides	"	"
Isothiocyanates	"	"
Sulfoxides	"	"
Sulfinic Acids	"	"
Alkyl Sulfonic Acids	1×10^{-3}	2.5×10^{-4}
Alkyl Sulfonic Acids	"	"

In several cases, larger portions of filters were analyzed for the sulfur compounds listed above. Negative results were also obtained in these instances. It is quite probable therefore that the emission rates of these compounds if they exist at all in auto exhaust are probably several orders of magnitude below those rates listed in Table IV-8. Limited sample sizes were necessary because of the large number of different analyses that were made on the particulate filters.

On the basis of the results, it appears that no significant quantities of organic sulfur compounds are emitted from catalysts under these test conditions.

IV.2 Exhaust Metal Particulate Emission Rates

The emission rates of the following metals were measured on all of the test runs:

Ca, Al, Zn, Cr, Fe, Cu, Ni, Pb, and Pt.

Although referred to as metals, the above exhaust components with the possible exception of platinum would not be likely to exist in their elemental state. Both analytical methods (emission spectroscopy and X-ray fluorescence) do not distinguish whether the above exist in the metallic or combined state. The analytical techniques are discussed in detail in Section A.5 of Appendix A.

It is most likely that the above metals when present in exhaust exist as oxides, sulfates, or mixed oxy-sulfates. No attempt was made to determine the types of metallic compounds.

The metal derived particulate emissions will hereinafter be referred to as metal oxides. This term is used simply for convenience and to indicate that the metal emissions do not exist as the free metals. It is not meant to imply that the oxide is the only combined form of the metal.

IV.2.1 Metal Oxide Emissions Under 1975 FTP Conditions

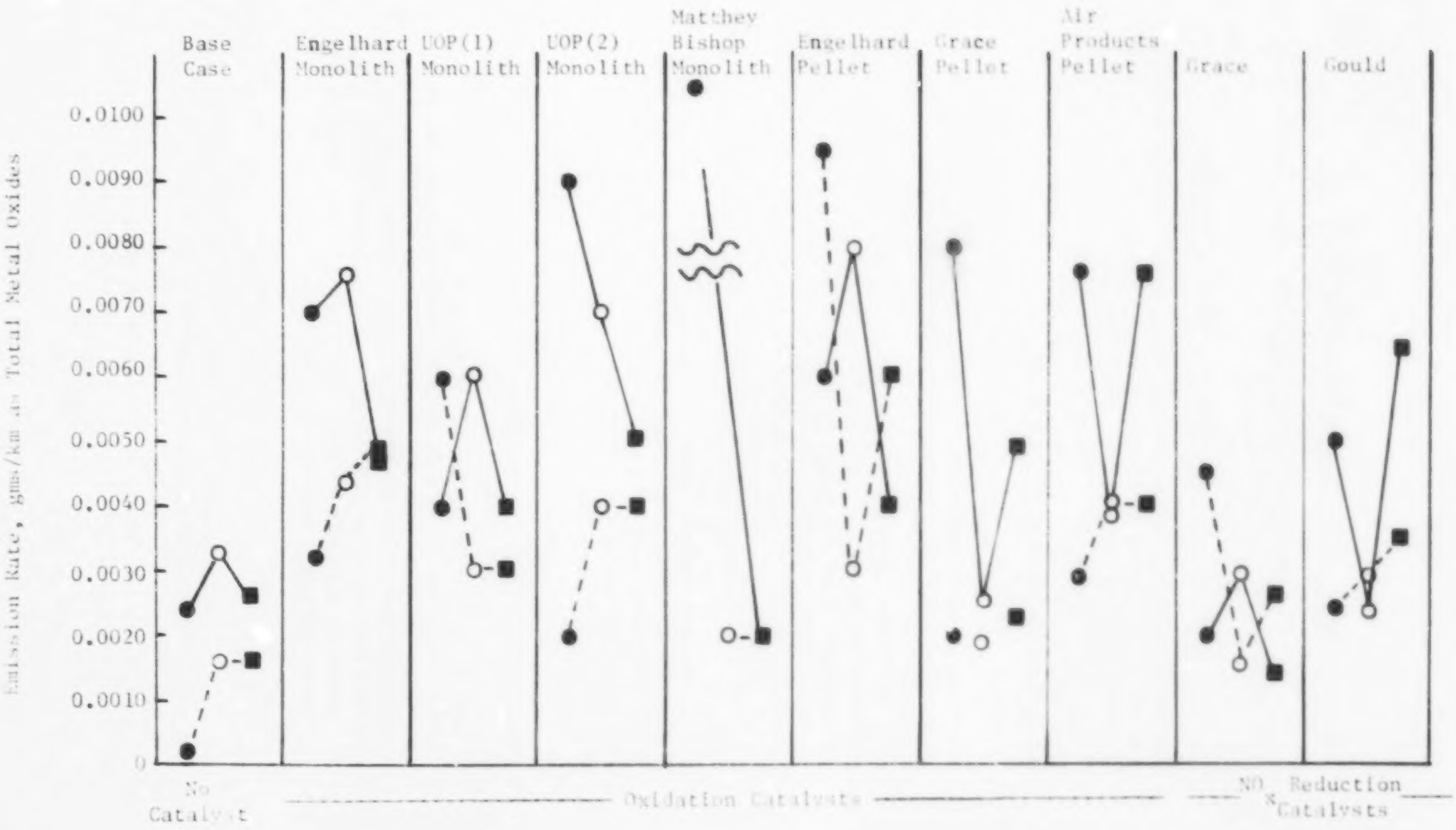
The detailed metal emission data are presented in Appendix E. Figure IV-30 shows the metal emission rates on the 1975 FTP's calculated as total metal oxides for the base case vehicle and for the vehicle equipped with the various catalysts. Both initial and final FTP emission rates are shown for each fuel sulfur content.

The total metal oxide emission rates are generally higher when the vehicle is equipped with oxidation catalysts ranging from about 0.0018 to 0.0110 gms/km on the 1975 FTP. Metal oxide emissions from the NO_x reduction catalysts ranged from about 0.0019 to 0.0064 gms/km. The lowest metal oxide emissions were observed with the base case vehicle. The range in this case was from 0.0002 to 0.0033 gms/km. There does not appear to be any dependence of metal oxide emission rate with fuel sulfur level (or correspondingly sulfate emissions), whether the vehicle is tested in the conventional mode, or equipped either with oxidation or reduction catalysts on the 1975 FTP.

The increased metal oxide emissions from catalyst vehicles can probably be associated with attrition from the catalyst system. The differences exhibited between oxidation catalysts and NO_x reduction catalysts may be due to attrition being greater under the leaner conditions (higher oxidation potential) that would prevail with these systems.

FIGURE IV-30

TOTAL METAL OXIDE EMISSION RATES, **gms/km** OBTAINED WITH INDICATED CATALYST, INITIAL AND FINAL 1975 FTP ON EACH TEST FUEL; (—— = INITIAL, ---- = FINAL FTP)
● = 0.019% S, ○ = 0.110% S, ■ = 0.091% S



IV.2.2 Metal Oxide Emissions Under Cruise Conditions, Relation to Sulfate Emissions

As sulfate emissions were higher on the 64 km/hr. and 96 km/hr. cruises, it was of interest to see if the metal oxide emission rates could be correlated with sulfate emissions (fuel sulfur content). Figures IV-31 to IV-39 show the total metal oxide emission rates as a function of fuel sulfur content for the 64 and 96 km/hr. cruises. The sum of the metal particulates are usually less than 5 to 10% of the sulfate emissions.

Generally, the sum of the metal emission rates on a given run with an oxidation catalyst vehicle are a small fraction of the sulfate emissions. However, on the FTP's with the 0.019 wt.% sulfur fuel, the metal emission rates exceeded the sulfate emission rates. This is primarily due to the fact, as discussed above, that metal oxide emissions are higher on the FTP's than on steady state cruises. When this phenomenon is coupled with the fact that sulfate storage is more favorable on the FTP than on the steady state cruises, it is not surprising that the metal oxide emission rates, however low, could exceed the H_2SO_4 emission rates when an oxidation catalyst equipped vehicle is operating on a low sulfur fuel under cyclic driving conditions. Table IV-8 shows the relative emission rates of metal oxide to sulfates for the vehicle equipped with the various ocidation catalysts on the cyclic and steady state cruises, operated on the three test fuels. The FTP values are the averages of the initial and final FTP's of the test sequence.

There does not appear to be any direct relationship between fuel sulfur content and metal oxide emissions. Indeed, with the exception of the Air Products pelleted oxidation catalyst (Figure IV-37), the metal oxide emissions from the vehicle operating on the low sulfur fuel are generally higher or comparable to those observed when a high sulfur test fuel is used. These results should not be taken to mean that some type of inverse relationship exists between metal oxide emissions and sulfate emissions (related linearly to fuel sulfur content), but rather that other factors are operating. No systematic assessment of these factors was made. However, tentative conclusions may be drawn regarding the influence of some of the variables encountered on metal oxide emission rates.

For example, the metal oxide emission rates are generally higher on the 1975 FTP's than on the steady state cruises. This applies to both the initial and final FTP's,indicating that accelerations and decelerations are the major factors responsible for the production of these types of emissions.

With several exceptions, the emission rates on the first FTP were higher than the final FTP. This may be due to purging of the exhaust by the first FTP, idle, and cruise tests prior to the final FTP. Assuming that purging is responsible for the lower emission rates obtained on the final FTP, the fact that the FTP emission rates generally are higher than the steady state cruise emission rates supports the hypothesis that accelerations and decelerations are the most important factors influencing metallic particulate emissions.

IV.2.3 Emission Rates of Specific Metals

Analyses for specific metals were carried out in order to determine how the presence of catalysts alters the emission pattern of metal-derived particulate. The effect of the catalyst on metal-derived particulate matter can occur by way of catalyst, substrate attrition, or both, and/or by reaction between catalytically produced exhaust components and the exhaust system. For example, catalytically produced sulfuric acid could react with the walls of the exhaust system, with some of the surface reaction products then becoming entrained in the

FIGURE IV-31

METAL OXIDE EMISSION RATES, gms/km VS.
FUEL SULFUR, WT.% ON STEADY STATE CRUISES

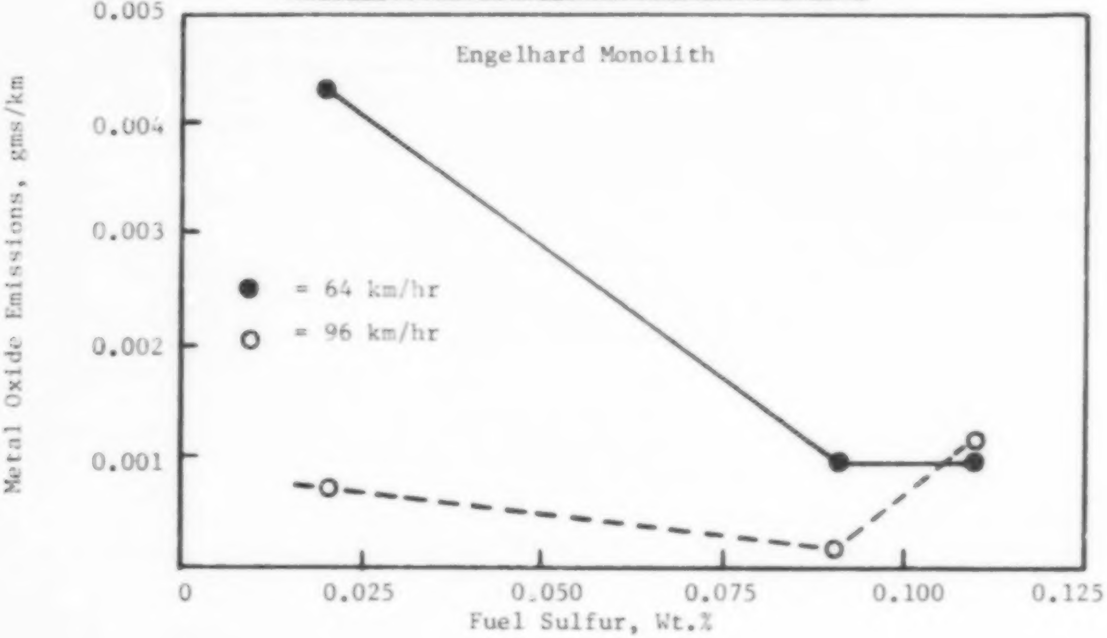


FIGURE IV-32

METAL OXIDE EMISSION RATES, gms/km VS.
FUEL SULFUR, WT.% ON STEADY STATE CRUISES

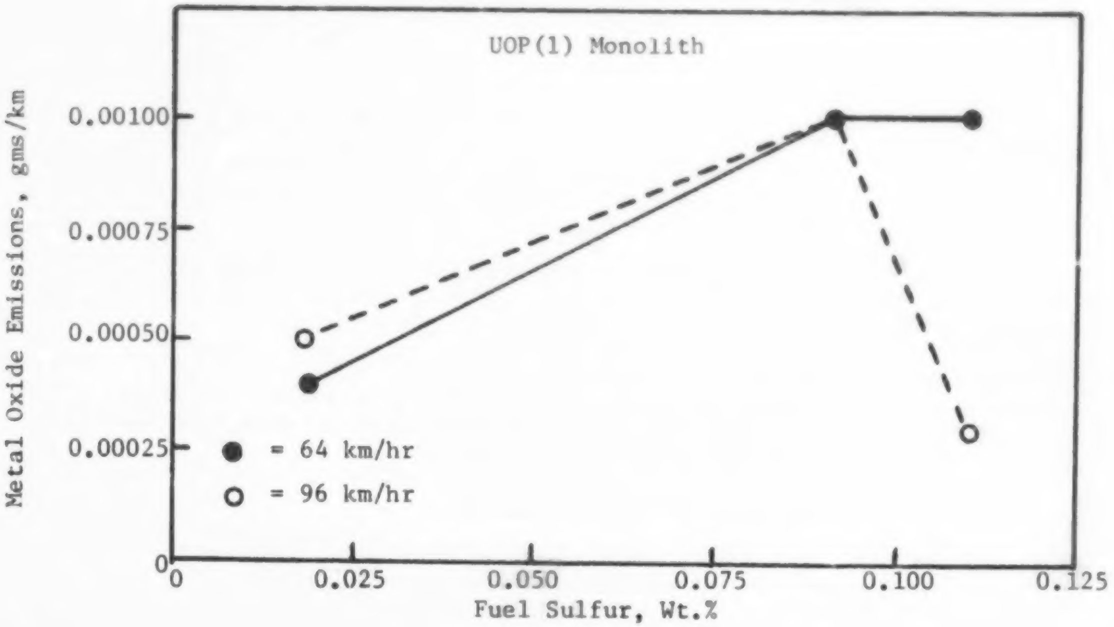


FIGURE IV-33

METAL EMISSION RATES, gms/km VS.
FUEL SULFUR, WT.% ON STEADY STATE CRUISES

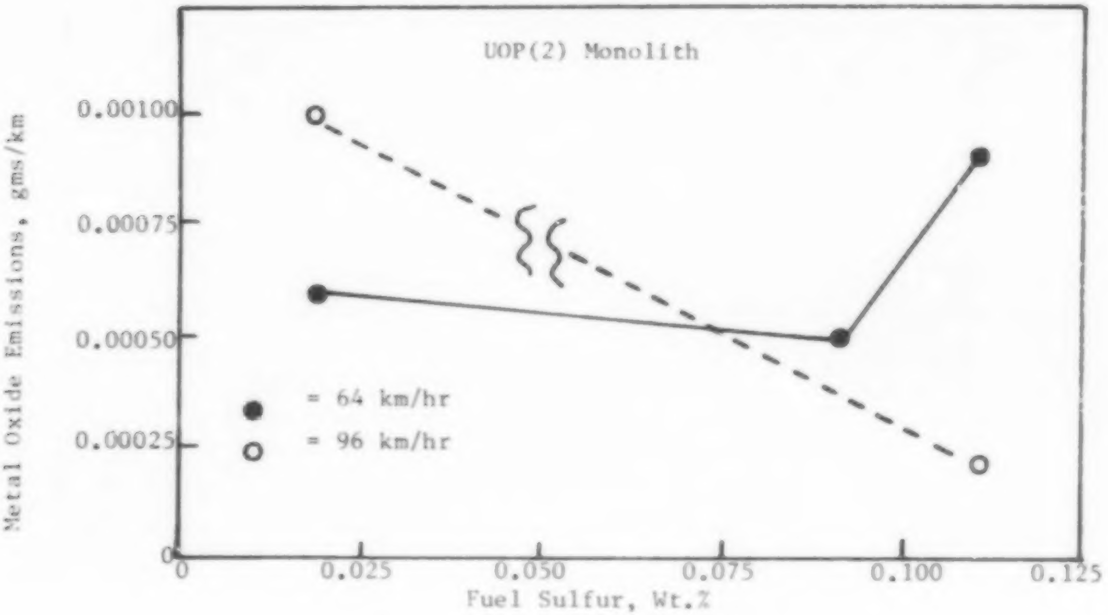


FIGURE IV-34

METAL OXIDE EMISSION RATES, gms/km VS.
FUEL SULFUR, WT.% ON STEADY STATE CRUISES

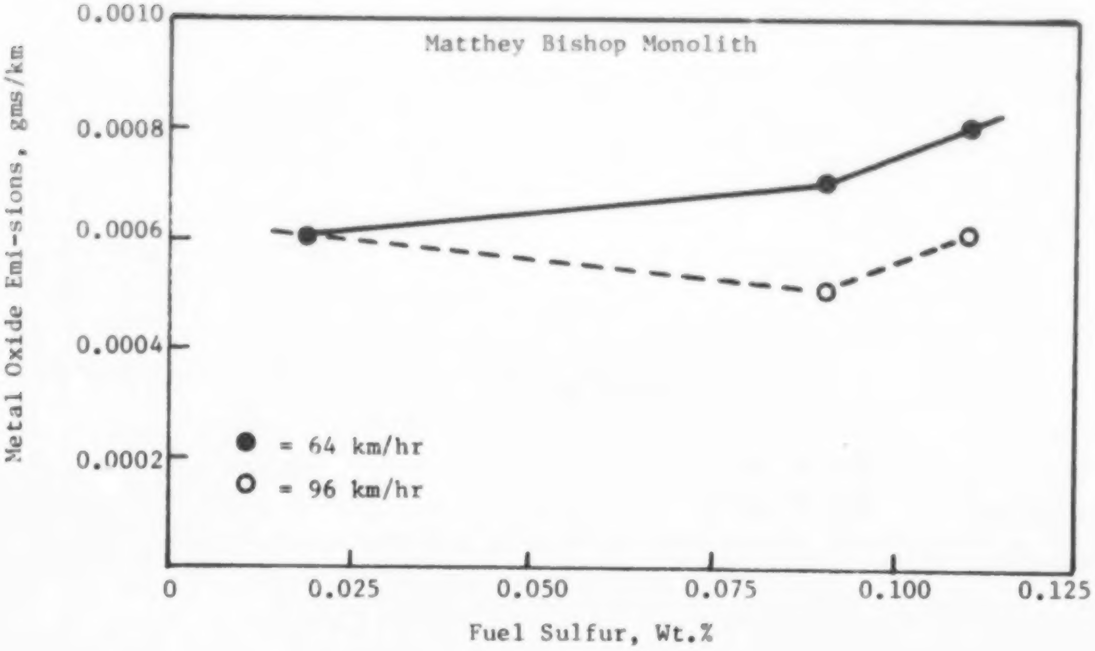


FIGURE IV-35

METAL OXIDE EMISSION RATES, gms/km VS.
FUEL SULFUR, WT.% ON STEADY STATE CRUISES

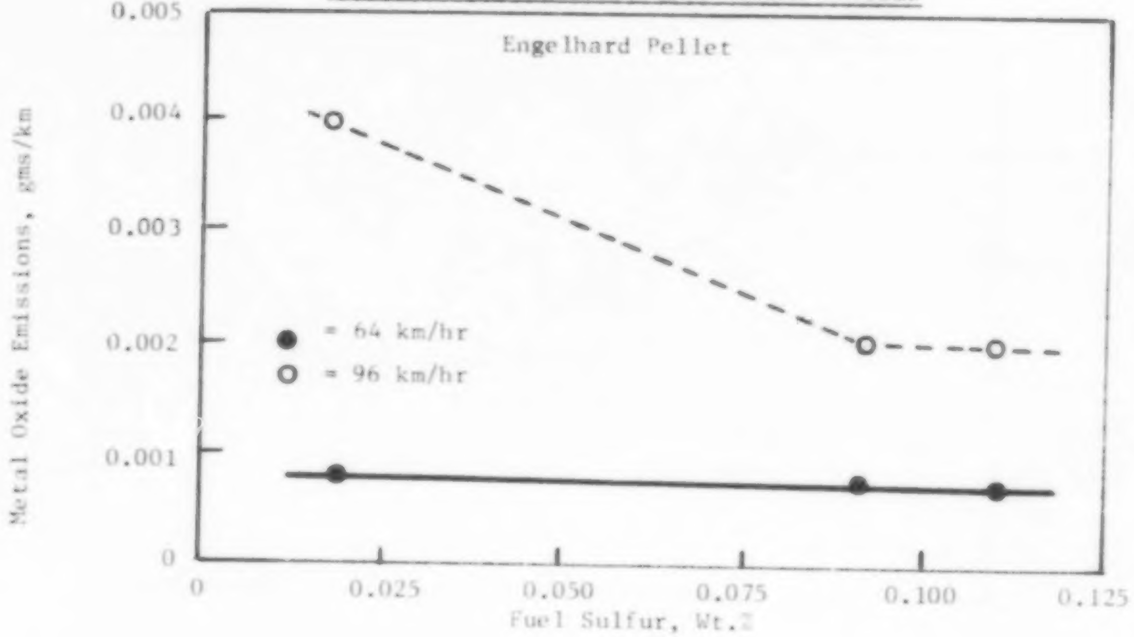


FIGURE IV-36

METAL OXIDE EMISSION RATES, gms/km VS.
FUEL SULFUR, WT.% ON STEADY STATE CRUISES

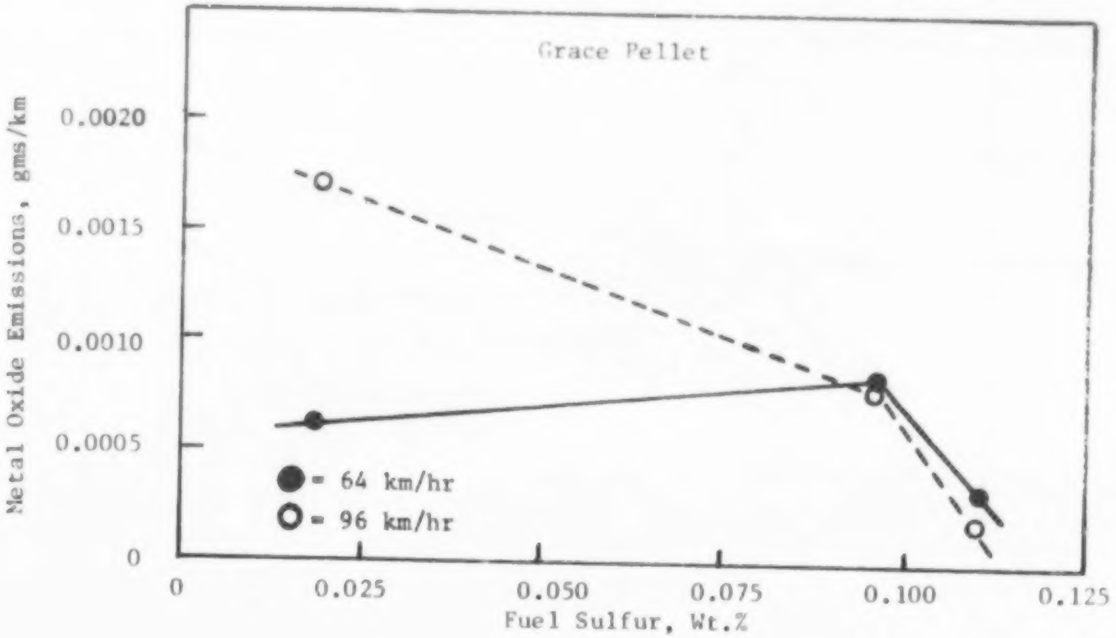


FIGURE IV-37

METAL OXIDE EMISSION RATES, gm/km VS.
FUEL SULFUR, WT.% ON STEADY STATE CRUISES

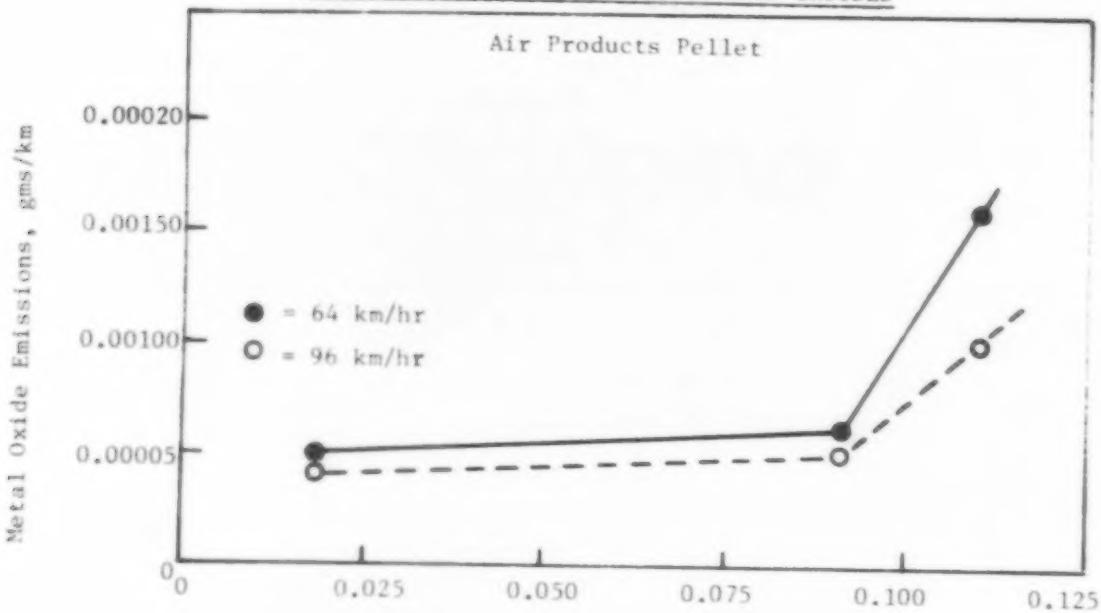


FIGURE IV-38

METAL OXIDE EMISSION RATES, gms/km VS.
FUEL SULFUR, WT.% ON STEADY STATE CRUISES

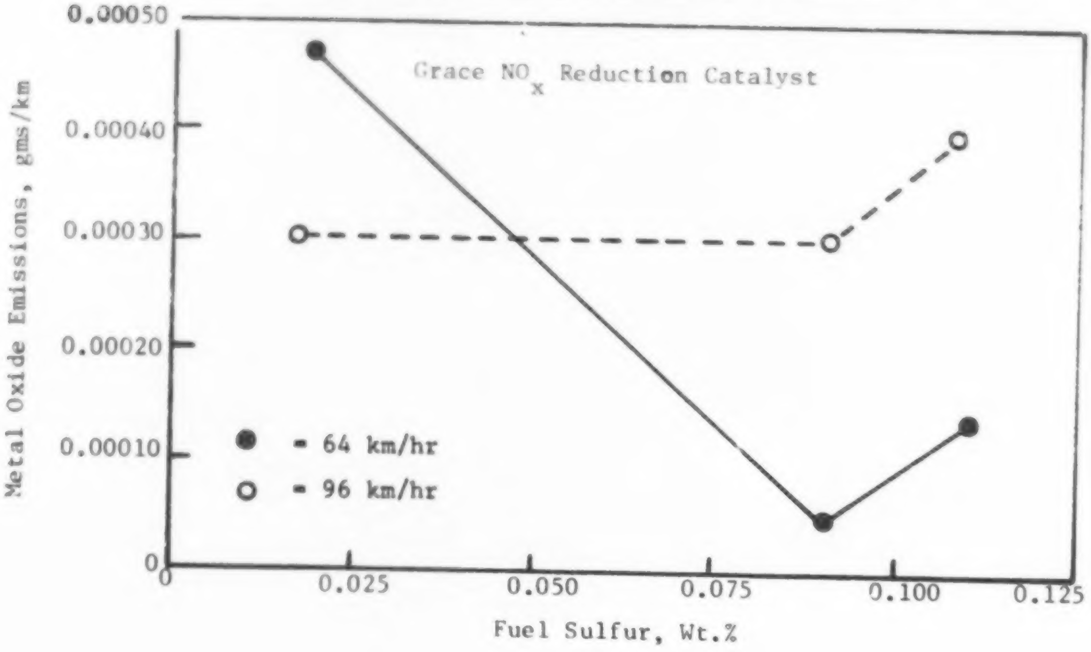


FIGURE IV-39

METAL OXIDE EMISSION RATES, **gms/km** VS.
FUEL SULFUR, WT.% ON STEADY STATE CRUISES

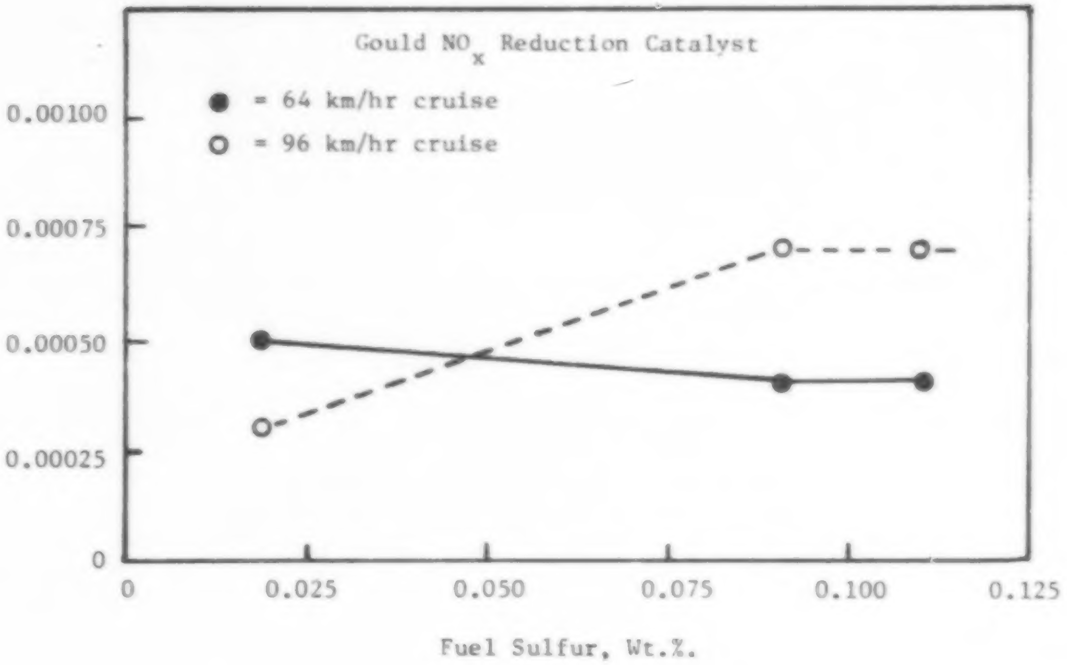


Table IV-8

Relative Emission Rates, Total Metal Oxides To Sulfates for Oxidation Catalyst Equipped Vehicles

		Total Metal Oxide Emissions as % of Sulfate Emissions on Indicated Vehicle Test		
Catalyst	% Fuel Sulfur	75 FTP	64 km/hr.	96 km/hr.
Engelhard Monolith	0.019	212	7	40
Engelhard Monolith	0.110	10	1	2
Engelhard Monolith	0.091	8	<1	2
UOP (1)	0.019	367	3	5
UOP (1)	0.110	10	<1	<1
UOP (1)	0.091	25	<1	2
UOP (2)	0.019	88	4	4
UOP (2)	0.110	13	<1	<1
UOP (2)	0.091	7	<1	-
Matthey Bishop	0.019	367	10	6
Matthey Bishop	0.110	19	2	<1
Matthey Bishop	0.091	11	2	1
Engelhard Pellet	0.019	325	80	15
Engelhard Pellet	0.110	55	<1	2
Engelhard Pellet	0.091	63	<1	<1
Grace Pellet	0.019	215	10	9
Grace Pellet	0.110	42	<1	<1
Grace Pellet	0.091	29	1	<1
Air Products Pellet	0.019	63	4	2
Air Products Pellet	0.110	10	2	1
Air Products Pellet	0.091	19	<1	<1

exhaust stream. This could result in an increase in the metallic content of exhaust particulate relative to conventional vehicles.

IV.2.3.1 Emission Rates of Platinum

Portions of the glass fiber filters were analyzed for platinum. In no case was platinum detected. Based on the detection limits of 0.35 μgms/cm^2, platinum emission rates must be below the following values for the vehicle tests shown below in Table IV-9.

TABLE IV-9
MAXIMUM POSSIBLE PLATINUM EMISSION RATES

Test	Maximum Possible Platinum Emission Rates, gms/km
1975 FTP	5.6×10^{-5}
64 km/hr., 1 hr.	1.6×10^{-5}
96 km/hr., 2 hrs.	5.2×10^{-6}

IV.2.3.2 Emission Rates of Aluminum

Figure IV-40 shows the aluminum emission rates on the initial 1975 FTP for the base case vehicle and for the vehicle equipped with the nine catalysts, for each of the three test fuels. It can be seen that the aluminum emission rates are generally higher when the vehicle is equipped with a catalyst indicating that some attrition of the catalyst substrate may have occurred. The maximum emission rate observed was with the Engelhard pelleted catalyst system, 0.00045 gms/km, which was about six times greater than the maximum rate observed with the unequipped vehicle.

The inability to detect platinum is consistent with the observed aluminum emission rates. For example, even at the highest aluminum emission levels observed,about 0.001 gms/km, the platinum could be as much as 5-6% of the aluminum content and still be below our platinum detection limits. Since the platinum content is well below 1% of the substrate, it should not be detected in auto exhaust particulate.

IV.2.3.3 Emission Rates of Lead

Figure IV-41 shows the lead emission rates for the base case vehicle, and when the vehicle was equipped with each of the nine catalysts on the initial 1975 FTP for each test fuel.

FIGURE IV-40

ALUMINUM EMISSION RATES, gms/km OBTAINED WITH INDICATED CATALYST, INITIAL 1975 FTP, ● = 0.019% S, ○ = 0.110% S, ■ = 0.091% S

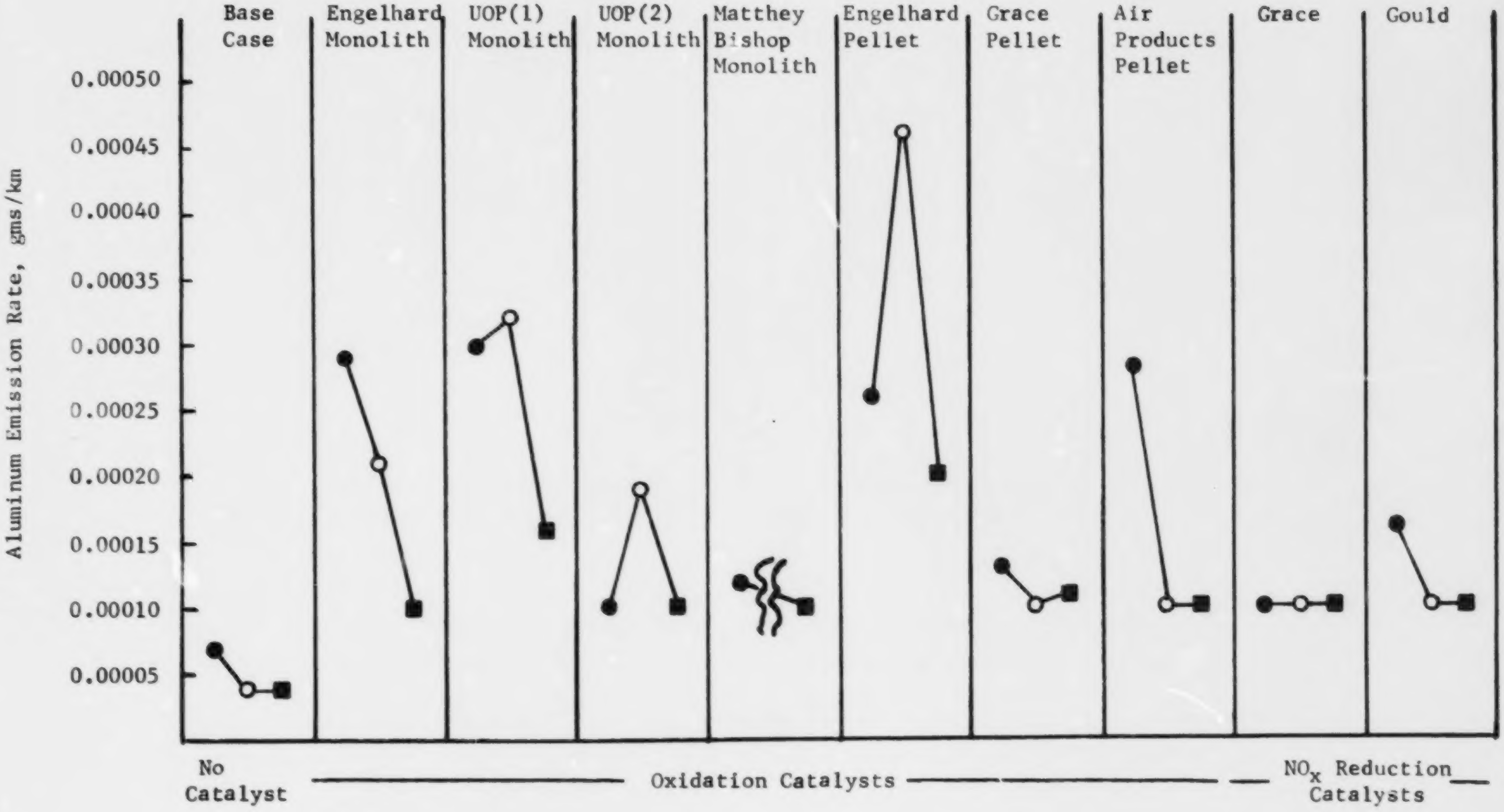
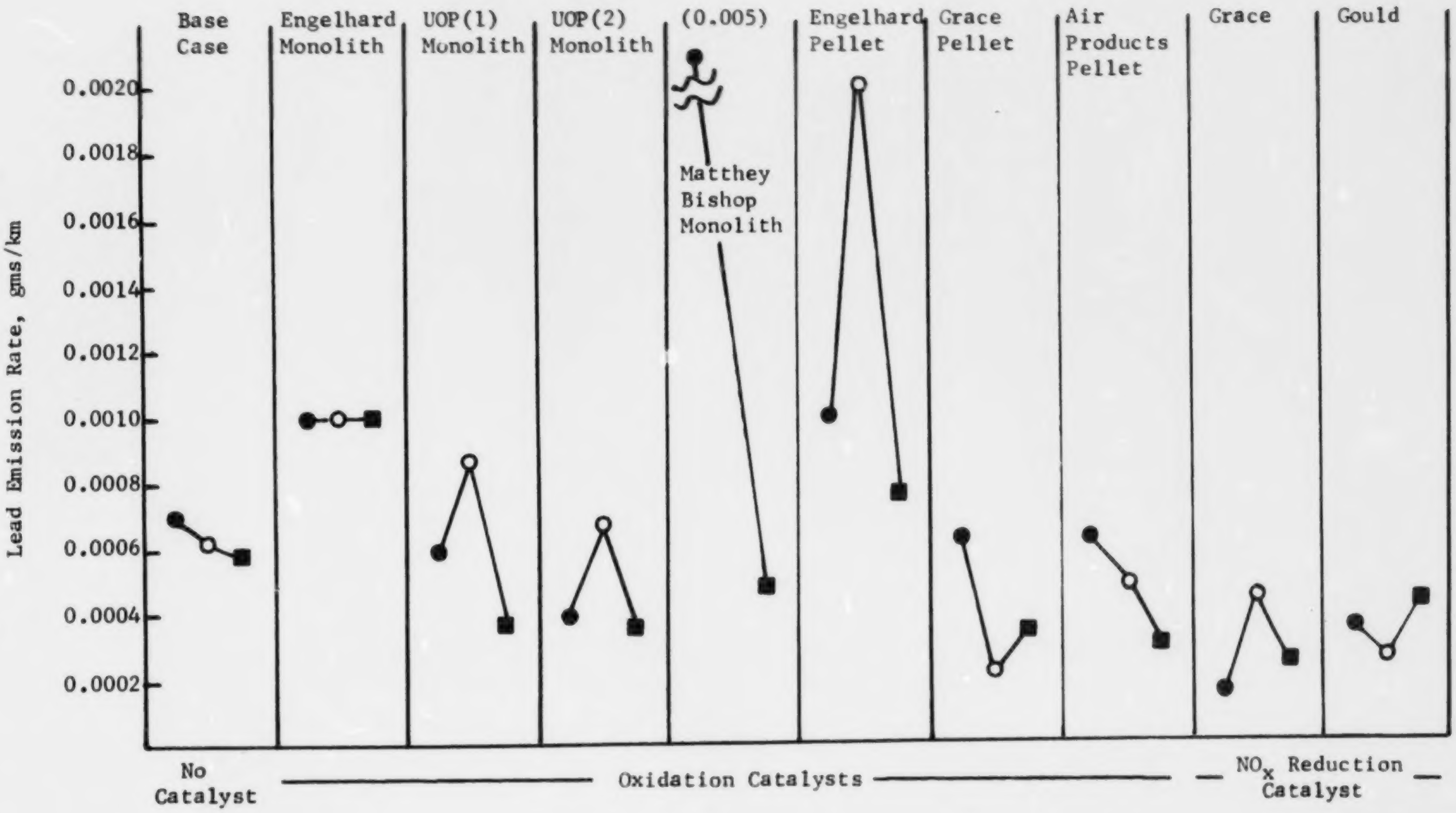


FIGURE IV-41

LEAD EMISSION RATES, gms/km OBTAINED WITH INDICATED CATALYST, INITIAL FTP, ● = 0.019% S, ○ = 0.110% S, ■ = 0.091% S



With the exception of the FTP's with the Matthey-Bishop monolith and the Engelhard pelleted system, the lead emission rates of the vehicle equipped with the other catalyst systems was indistinguishable from those of the base case vehicle. It would be expected that the lead emission rates would be independent of whether or not the vehicle was equipped with a catalyst since the leaded particulate, unlike the other metallic particulates, is ultimately fuel derived. Previous studies with production vehicles operating on leaded fuels have shown that the lead emission rate measured at any instant of time in the life history of a vehicle is not necessarily representative of the average amount of lead emitted over its lifetime (23).

Figure IV-42 shows the lead emission rates for the base case vehicle, and for the catalyst vehicle on the second FTP. It can be seen that, in general, the lead emissions are lower on the second FTP of the test sequence. The lead emission rate from the Engelhard pelleted catalyst-equipped vehicle is still higher than the base case vehicle or when the vehicle is equipped with the other catalysts, excepting the Engelhard monolith.

The higher lead emissions from the Engelhard pelleted catalyst-equipped vehicle may be due to its greater storage capability than other catalytic systems,so that it emits more leaded particulate than the other systems when conditions are favorable for release. The increased lead particulate emissions exhibited by the Engelhard monolith-equipped vehicle may be due to an unrepresentative erratic release.

The high lead emissions obtained with the Engelhard monolith could also be related to failure of a previous Engelhard system as a result of misfire under high speed cruise. This resulted in catalyst temperature above 1100°C for about 10 minutes. The test was terminated, new plugs installed, and the vehicle checked out.

A 1975 FTP the following day (Run No. 35, Appendix E) showed that the catalyst had become deactivated as evidenced by considerably higher CO, hydrocarbon, and SO_2 emissions than the initial FTP (Run No. 31, Appendix E). The lead emission rates on the FTP with the deactivated catalyst were the highest obtained in all the test runs except for one run with the Matthey-Bishop catalyst. The leaded particulate may have been driven off the catalyst substrate during failure of the catalyst deposited downstream, and a portion emitted on the FTP run with the deactivated catalyst.

The lead emission rates shown in Figures IV-42 to IV-43 are for the vehicle re-equipped with a new Engelhard monolith which was subjected to an accelerated conditioning in order to remain on schedule. The higher lead emission rates observed with this catalyst may be due to entrained exhaust lead deposits that were present in the exhaust system as a result of failure of the previous catalyst.

FIGURE IV-42

LEAD EMISSION RATES, gms/km OBTAINED WITH INDICATED CATALYST, 1975 FTP, ● = 0.019% S, ○ = 0.110% S, ■ = 0.091% S

(* Filter of Second FTP for Matthey Bishop Sent to EPA for Analysis)

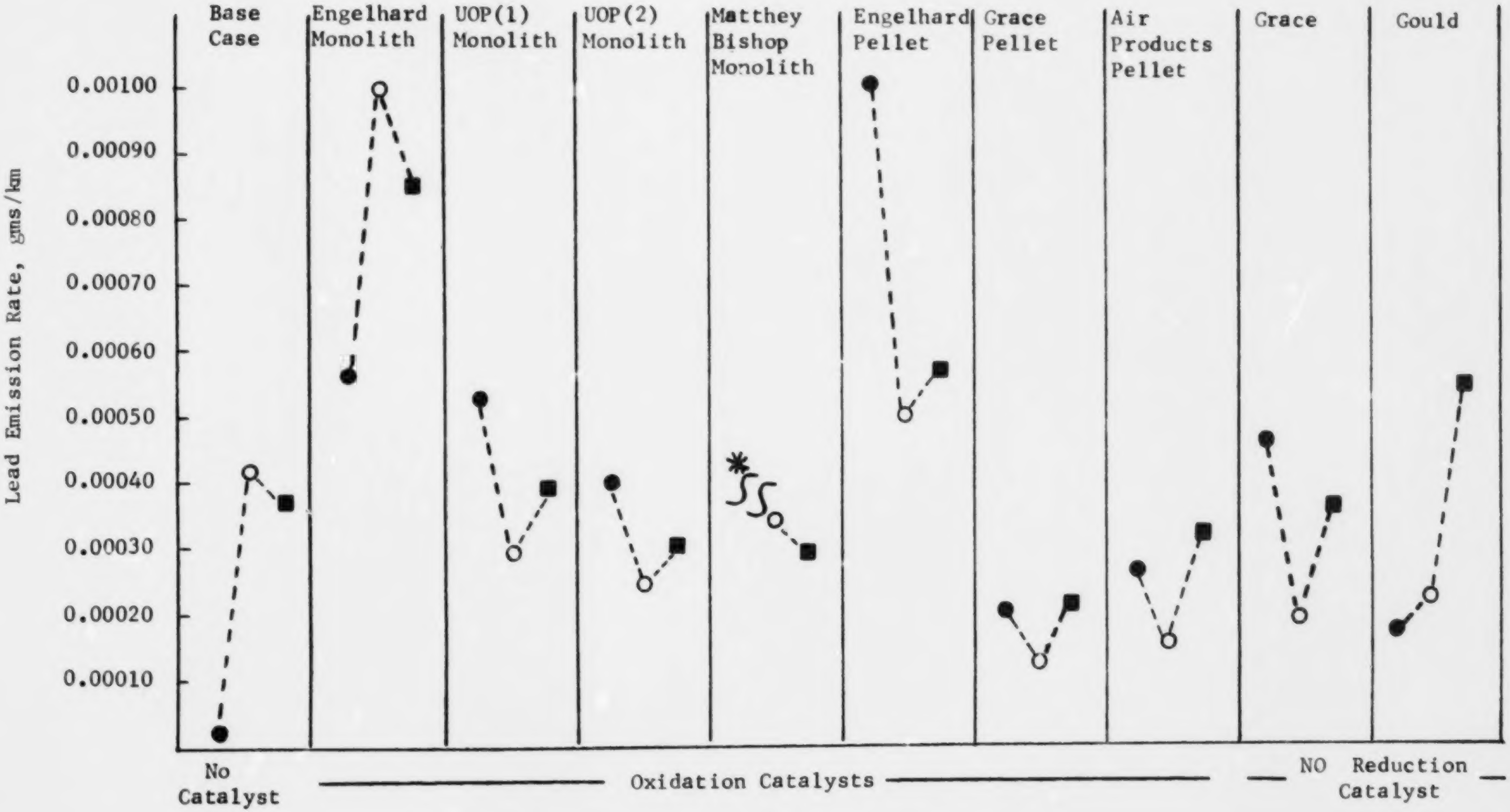
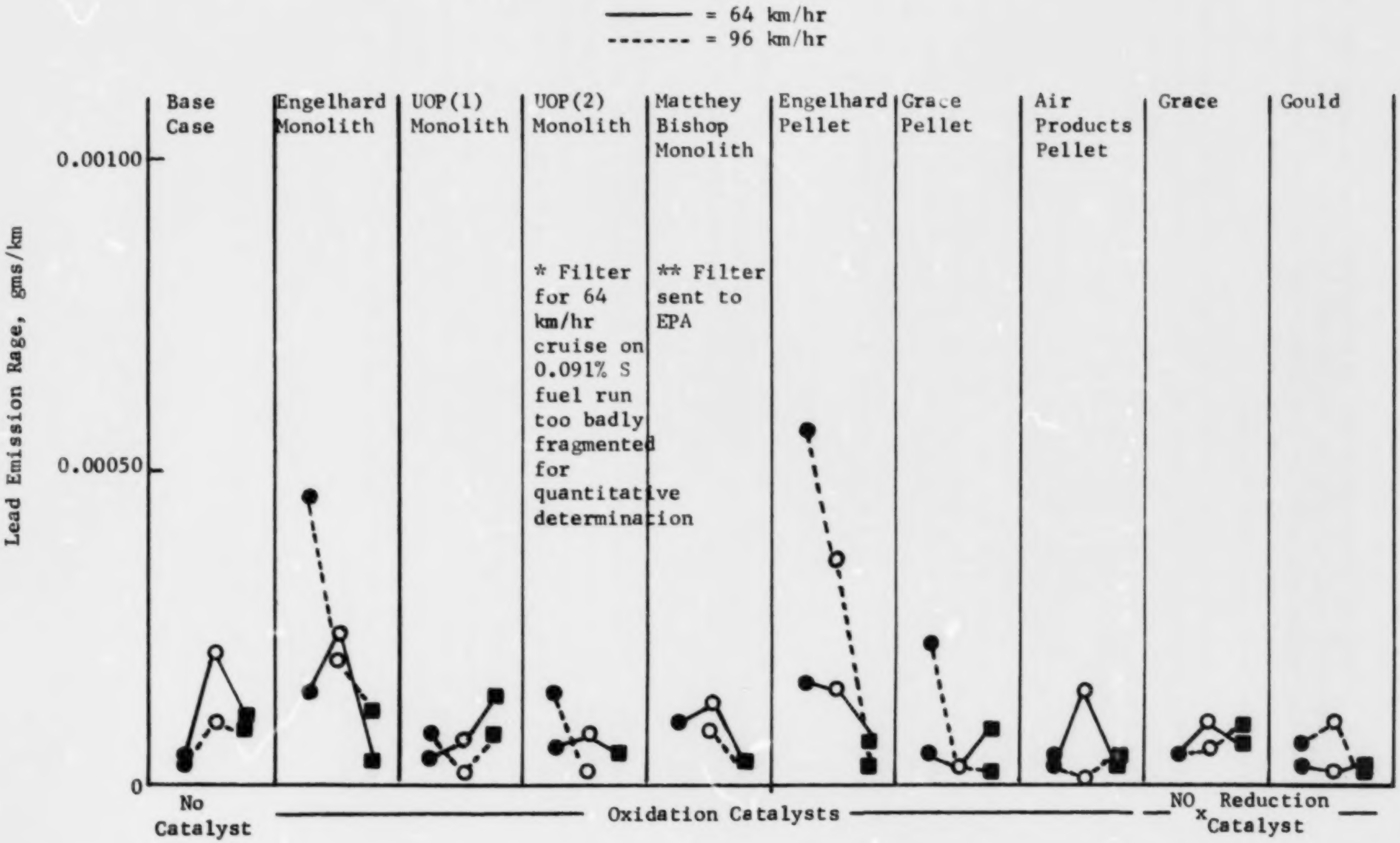


FIGURE IV-43

LEAD EMISSION RATES AT 64 AND 96 km/hr CRUISE OBTAINED WITH INDICATED CATALYST, ● = 0.019% S, ○ = 0.110% S, ■ = 0.091% S



* Filter for 64 km/hr cruise on 0.091% S fuel run too badly fragmented for quantitative determination

** Filter sent to EPA

Figure IV-43 shows the lead particulate emission rate for all catalyst-fuel combinations on the 64 and 96 km/hr. cruises. It can be seen that excepting both the monolithic and pelleted Engelhard catalyst runs, the lead emissions from the other catalyst runs were indistinguishable from the base case vehicle runs.

Generally, the emitted lead was considerably less than 50% of the lead burned. For example, with the unequipped vehicle, the emitted lead accounted for 10 to 23% of the lead burned on the FTP's. With the Engelhard pelletized oxidation catalyst, the emitted lead accounted for about 33% of the lead burned.

This agrees well with other workers (23) using a leaded fuel containing 3 grams of lead per gallon as motor mix. These workers found that the emitted lead accounted on the average for about 48% of the lead burned. It is reasonable to expect that if only about half of a much higher lead input can be accounted for, the emitted lead levels in our work should account for still smaller fractions of the lead input. For example, with the Grace pelletized oxidation catalyst-equipped vehicle, an average of about 9% of the input lead could be accounted for in the emissions for the 6 FTP's.

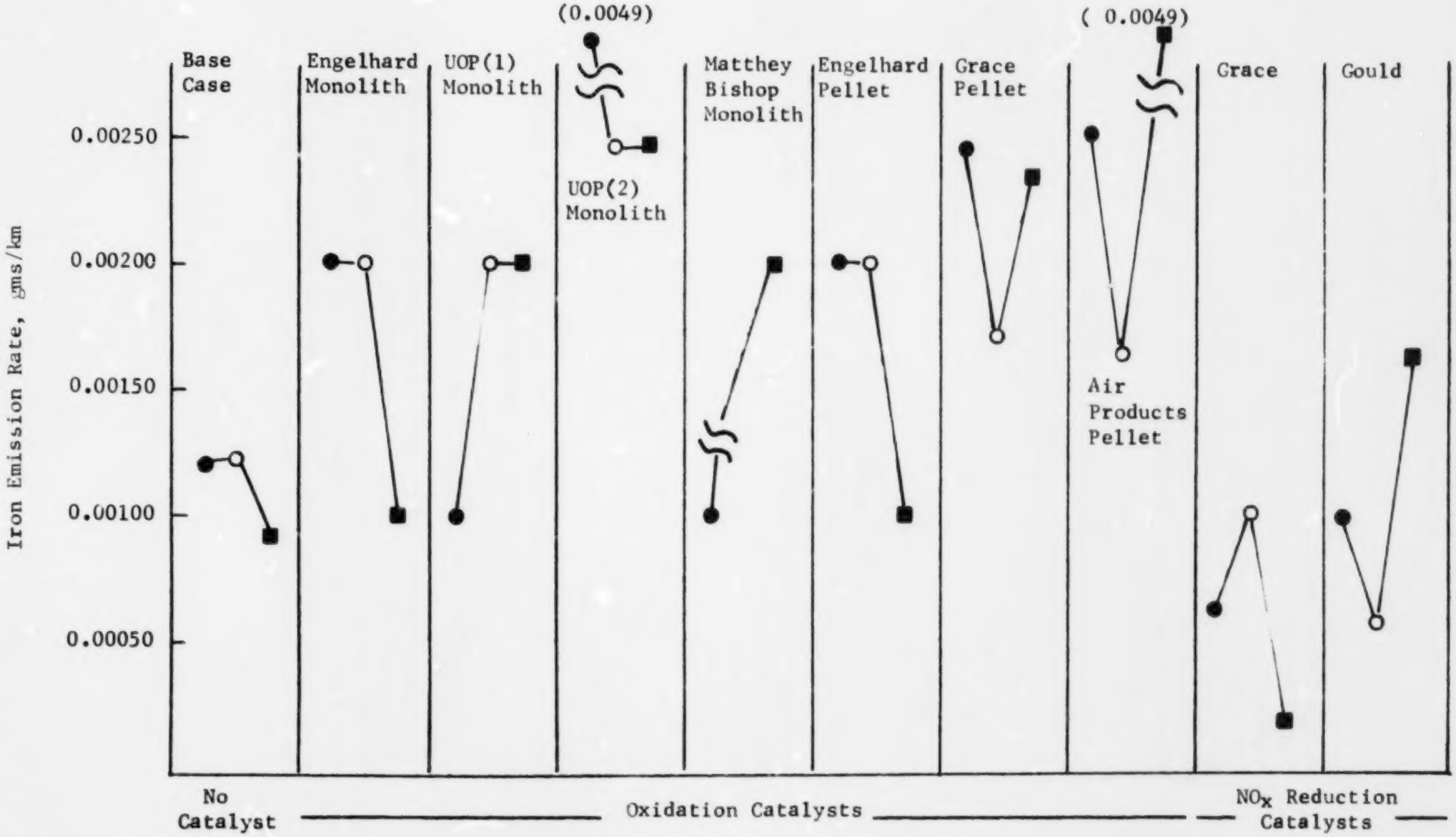
IV.2.3.4 Emission Rates of Iron

Figure IV-44 shows the iron emission rates obtained on the first 1975 FTP for the unequipped vehicle, and for the vehicle equipped with the various catalysts. As in the previous sections, the results are shown for each of the test fuels.

It can be seen that the emission rate of particulate iron is generally higher when the vehicle is equipped with oxidation catalysts than for the unequipped vehicle and the NO_x reduction catalyst-equipped vehicle. This suggests that the increase in iron emissions above the levels of the unequipped vehicle may be due to reaction of the exhaust system with catalytically produced sulfuric acid. However, it will be noted that the iron emission rate appears to be independent of the fuel sulfur content (or sulfate emission level). This may be due to a surface limited reaction of iron in the walls of the exhaust system with catalytically produced sulfuric acid. The increased iron emissions above the usual levels associated with engine and exhaust system wear is probably due to both factors (usual attrition plus reaction with sulfates) operating.

FIGURE IV-44

IRON EMISSION RATES, gms/km OBTAINED WITH INDICATED CATALYST
INITIAL 1975 FTP, ● = 0.019% S, ○ = 0.110% S, ■ = 0.091% S



IV.2.3.5 Emission Rates of Nickel

Figures IV-45 and IV-46 show the nickel emission rates on the first and second FTP's respectively for all vehicle-catalyst-fuel combinations. It can be seen that the nickel emission rates are independent of fuel sulfur content. The nickel emission rates of the base case vehicle was the same as when the vehicle was equipped with each of the seven oxidation catalysts, and with the Grace NO_x reduction catalyst. Dramatic increases in the nickel emission rates were observed when the vehicle was equipped with the Gould NO_x reduction catalyst.

These results with the Gould NO_x reduction catalyst are similar to what was obtained in earlier pre-contract work with Gould NO_x reduction catalysts (3). The nickel emission rates from the Gould NO_x reduction catalyst-equipped vehicle on the 1975 FTP ranged from 1×10^{-3} to values exceeding 2×10^{-3} gms/km. Earlier results on a somewhat different Gould NO_x reduction catalyst showed that on the 1972 FTP, nickel emission rates ranged from 2×10^{-3} to 8×10^{-3} gms/km.

The nickel emission rates on the steady state cruises were lower than FTP emission rates, as all metal derived particulate emissions were. However, differences between the Gould catalyst-equipped vehicle and the base case vehicle, and the vehicle equipped with the other catalyst systems are readily discernible. Steady state cruise nickel emissions with the Gould catalyst-equipped vehicle are 2 to 5 times higher than that observed with the other systems.

Preliminary A/F measurements on the test vehicle equipped with the Gould catalyst indicates that removal of the air pump was sufficient to produce net rich conditions as required for proper operation. However, detailed A/F measurements performed after the catalyst was conditioned and run through the program test sequence showed that the vehicle was operating in the lean mode. The increased nickel emissions, therefore, may be the direct result of improper lean operation.

IV.2.3.6 Emission Rates of Copper

Figures IV-47 and IV-48 shows the copper emission rates on the initial and final FTP's respectively for all catalyst-fuel combinations. The FTP copper emission rates are generally below 6×10^{-4} gms/km. Somewhat higher rates are observed with the Engelhard monolithic and pelleted catalyst system. These differences, if significant, may simply reflect the different levels of trace metals in the various catalyst systems.

FIGURE IV-45

NICKEL EMISSION RATES, gms/km OBTAINED WITH INDICATED CATALYST, INITIAL 1975 FTP, ● = 0.019% S, ○ = 0.110% S, ■ = 0.091% S

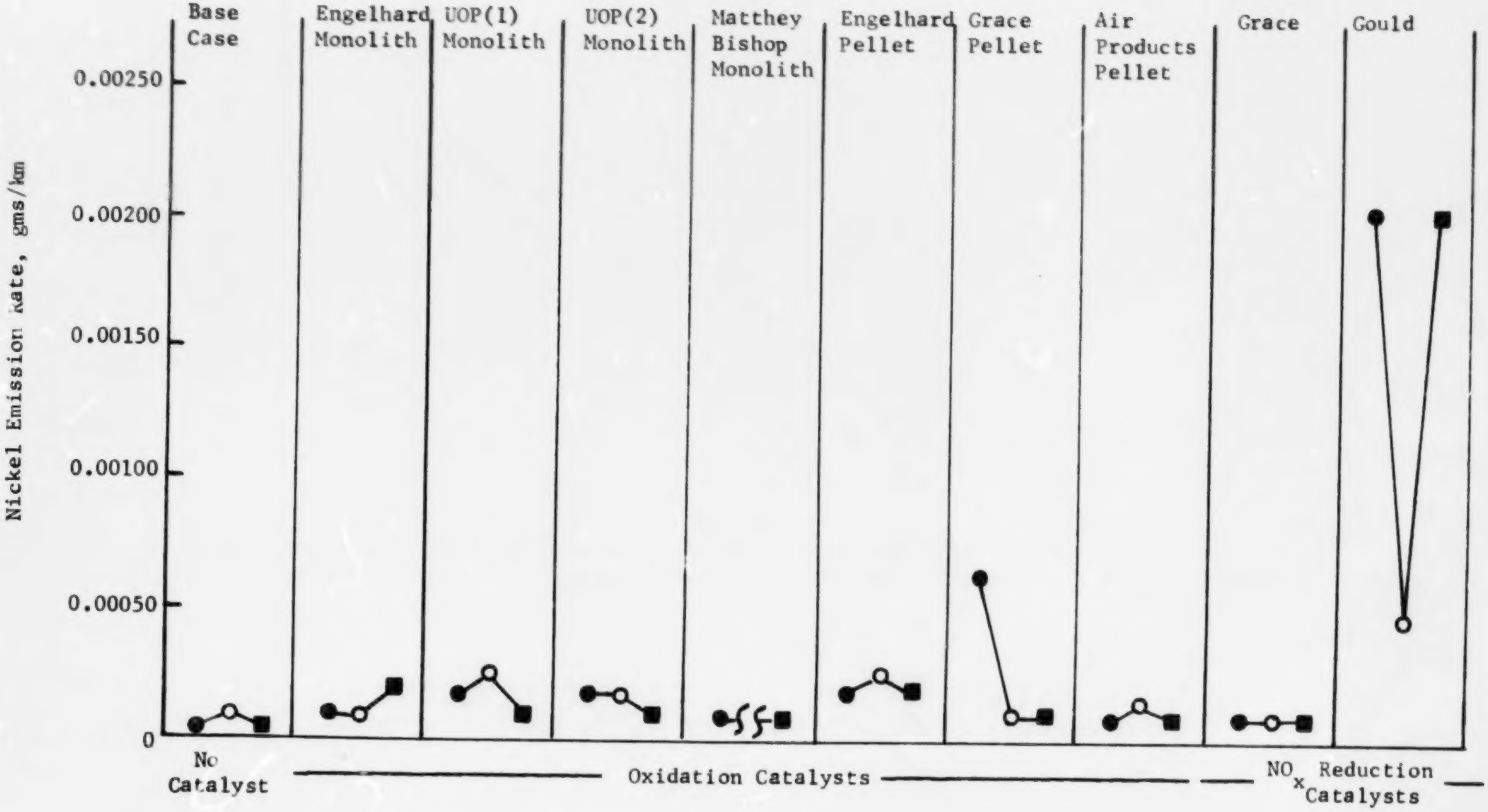


FIGURE IV-46

NICKEL EMISSION RATES, gms/km OBTAINED WITH INDICATED CATALYSTS, FINAL 1975 FTP, ● = 0.019% S, ○ = 0.110% S, ■ = 0.091% S

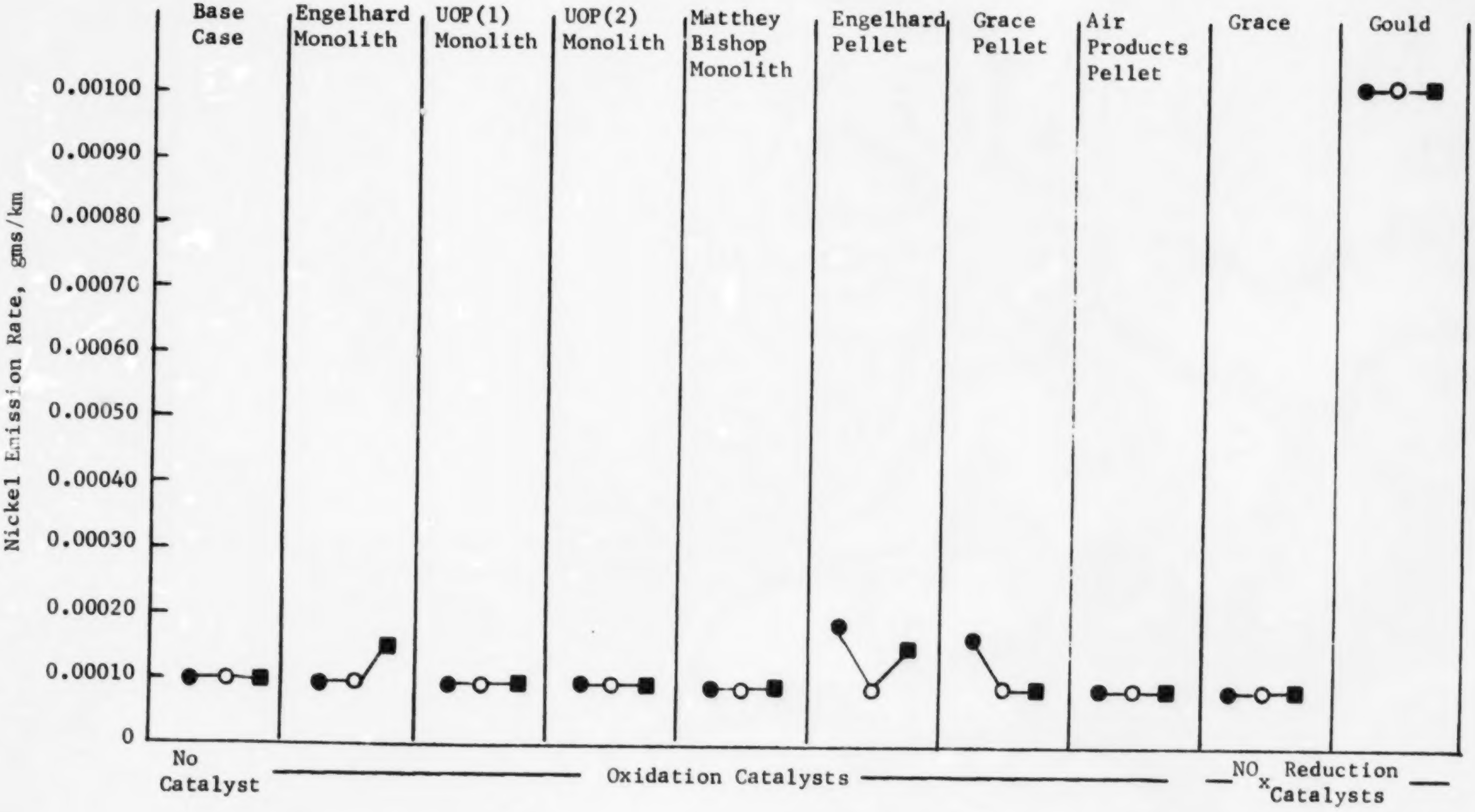


FIGURE IV-47

COPPER EMISSION RATES, gms/km OBTAINED WITH INDICATED CATALYST
INITIAL 1975 FTP, ● = 0.019% S, ○ = 0.110% S, ■ = 0.091% S

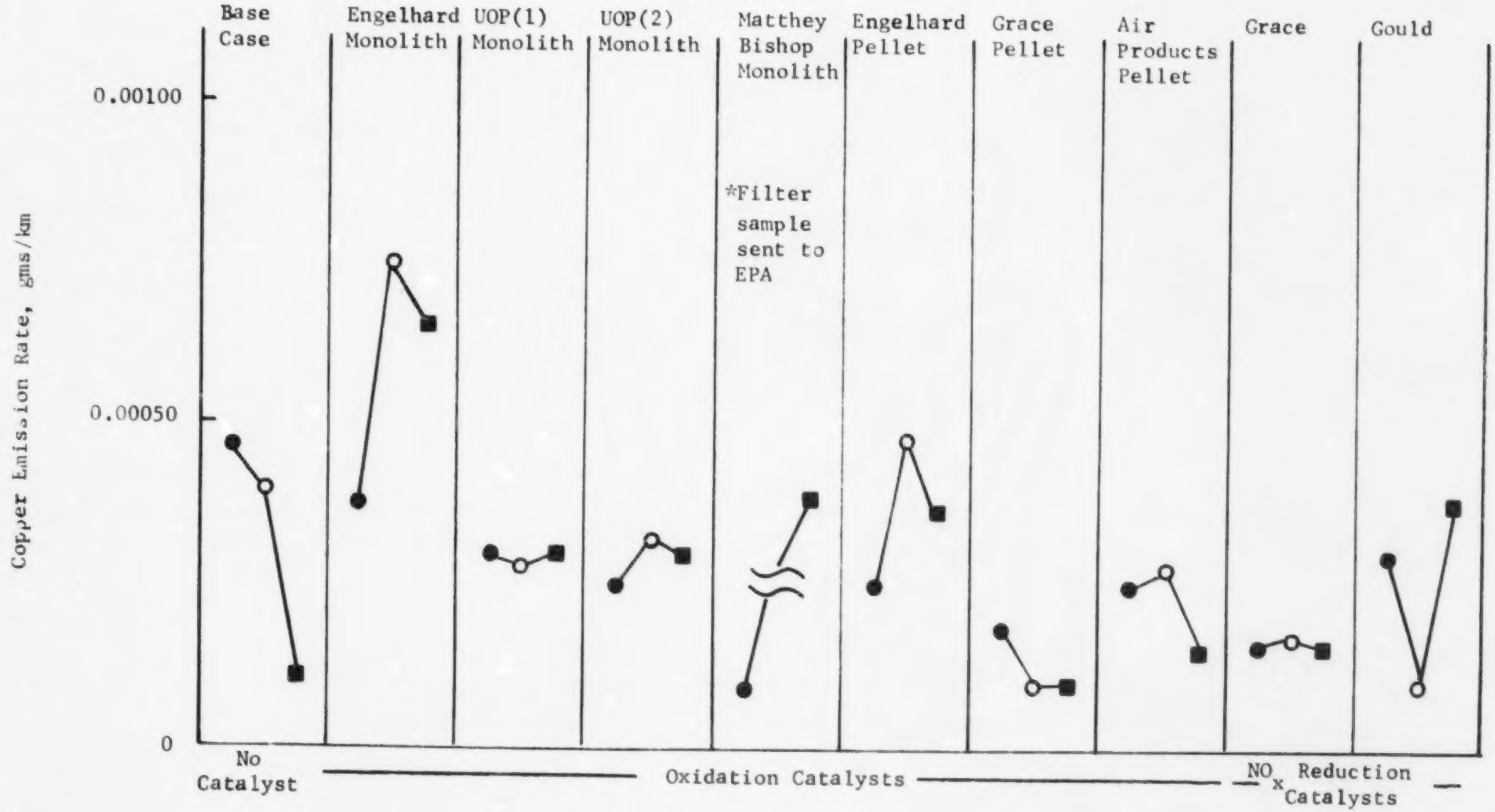
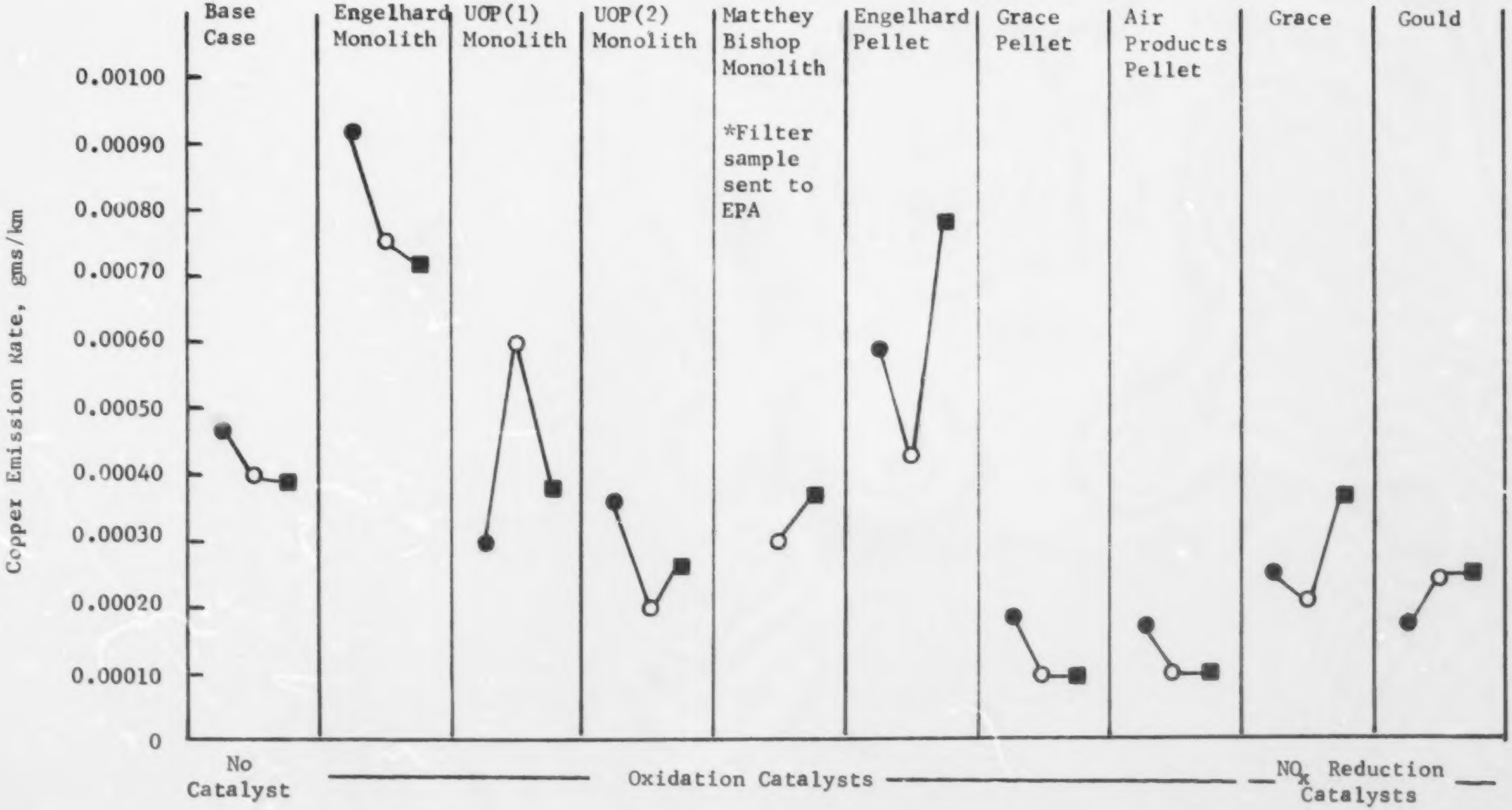


FIGURE IV-48

COPPER EMISSION RATES, gms/km OBTAINED WITH INDICATED CATALYST
FINAL 1975 FTP, ● = 0.019% S, ○ = 0.110% S, ■ = 0.091% S



IV.2.3.7 Emission Rates of Zinc

Figure IV-49 shows the zinc emission rates on the initial 1975 FTP for all catalyst fuel combinations. Although there seems to be no correlation between zinc emissions and fuel sulfur level, there does appear to be some correlation with the level of sulfate produced by a given catalyst. The lowest zinc emission rates were obtained with the base case vehicle and the vehicle equipped with the NO_x reduction catalysts, where little, if any, sulfuric acid is observed. There is not a one-to-one correspondence on a single run between the sulfuric acid emission and zinc emission rate. This could be due to the generally erratic pattern of metallic vehicular emissions. Thus, for example, the high zinc emissions observed in a given run may be zinc that corroded or reacted with sulfuric acid in an earlier or previous run. At other times, much of the emitted zinc may be that which had reacted with sulfuric acid generated in the same run. The source of the zinc emissions has not been traced, although the muffler system is a likely source. Zinc is also present in the lubricant.

IV.2.3.8 Emission Rates of Calcium

Calcium emission rates observed on the FTP shown in Figure IV-50 are independent of fuel sulfur level. With minor differences, the calcium emission pattern and level are the same both for all the catalyst systems and the base case vehicle. This would be expected if the calcium containing exhaust particulate was derived from the lubricating oil.

On the FTP's the calcium emission rates were of the order of 1×10^{-4} to 2×10^{-4} gms/km. The lubricating oil used contained about 0.16 and 0.21 wt. % calcium, equivalent to about 1.7 gms calcium per quart. Typical oil consumption rates for new vehicles is about 0.2 quart per 1600 km.

The calcium emission rate corresponding to this consumption rate is about 2.1×10^{-4} gms/km. This is in excellent agreement with the calcium emission rates shown in Figure IV-50, indicating that 25% to virtually all of the calcium associated with the consumed lubricating oil is emitted as exhaust particulate. As with the other metal derived exhaust particulate, steady state cruise calcium emission rates are lower than the FTP values, accounting for about 10 to 15% of the calcium.

IV.2.3.9 Emission Rates of Chromium

The chromium emission rates obtained on the initial FTP are shown in Figure IV-51. It can be seen that the chromium emission rates are independent of fuel sulfur content. Both Engelhard catalyst systems (monolith and pelletized) and the first UOP catalyst tested generally

FIGURE IV-49

ZINC EMISSION RATES, gms/km OBTAINED WITH INDICATED CATALYST, INITIAL 1975 FTP ● = 0.019% S, ○ = 0.110% S, ■ = 0.091% S

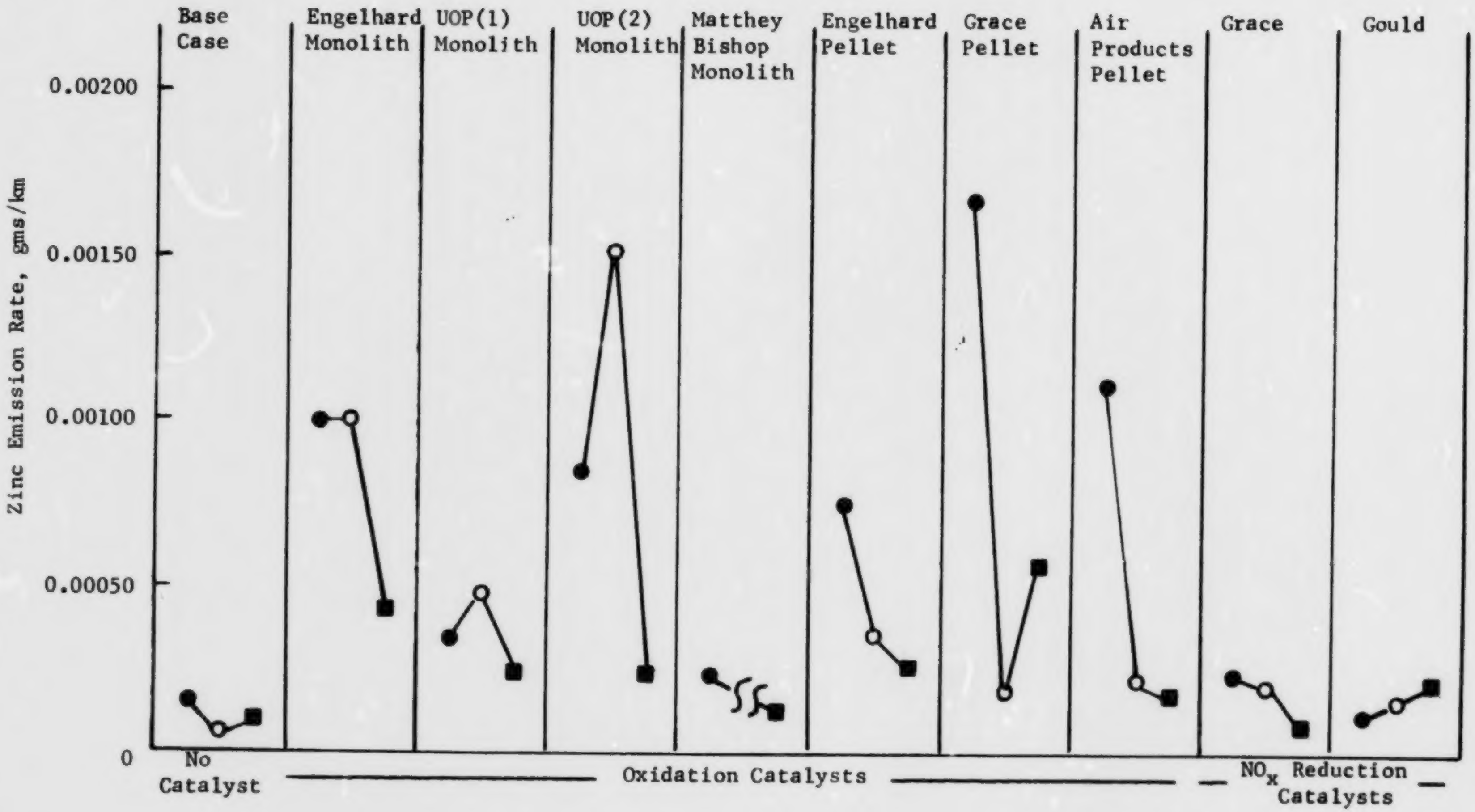


FIGURE IV-50

CALCIUM EMISSION RATES, gms/km OBTAINED WITH INDICATED CATALYSTS, INITIAL FTP, ● = 0.019% S, ○ = 0.110% S, ■ = 0.091% S

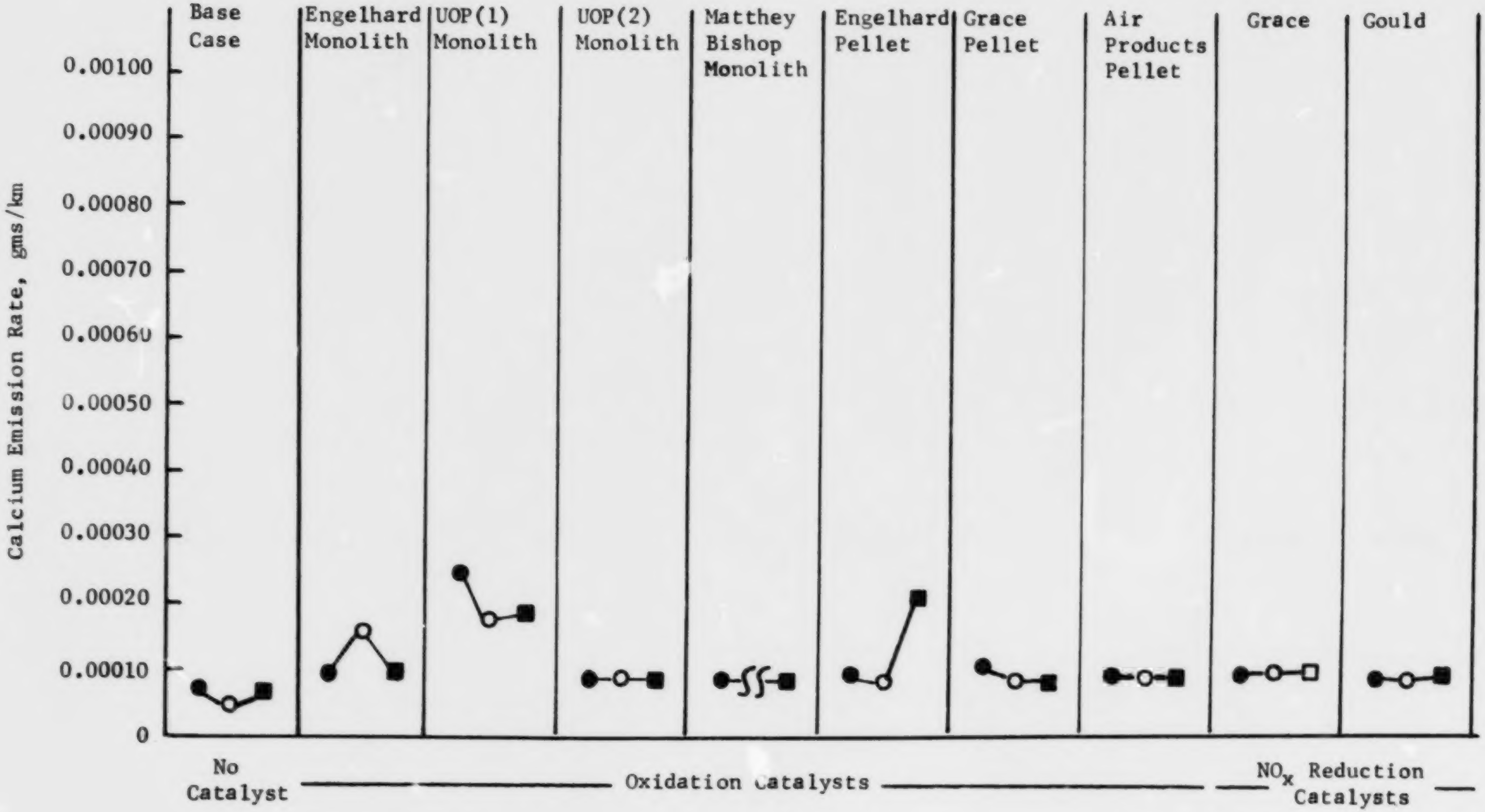
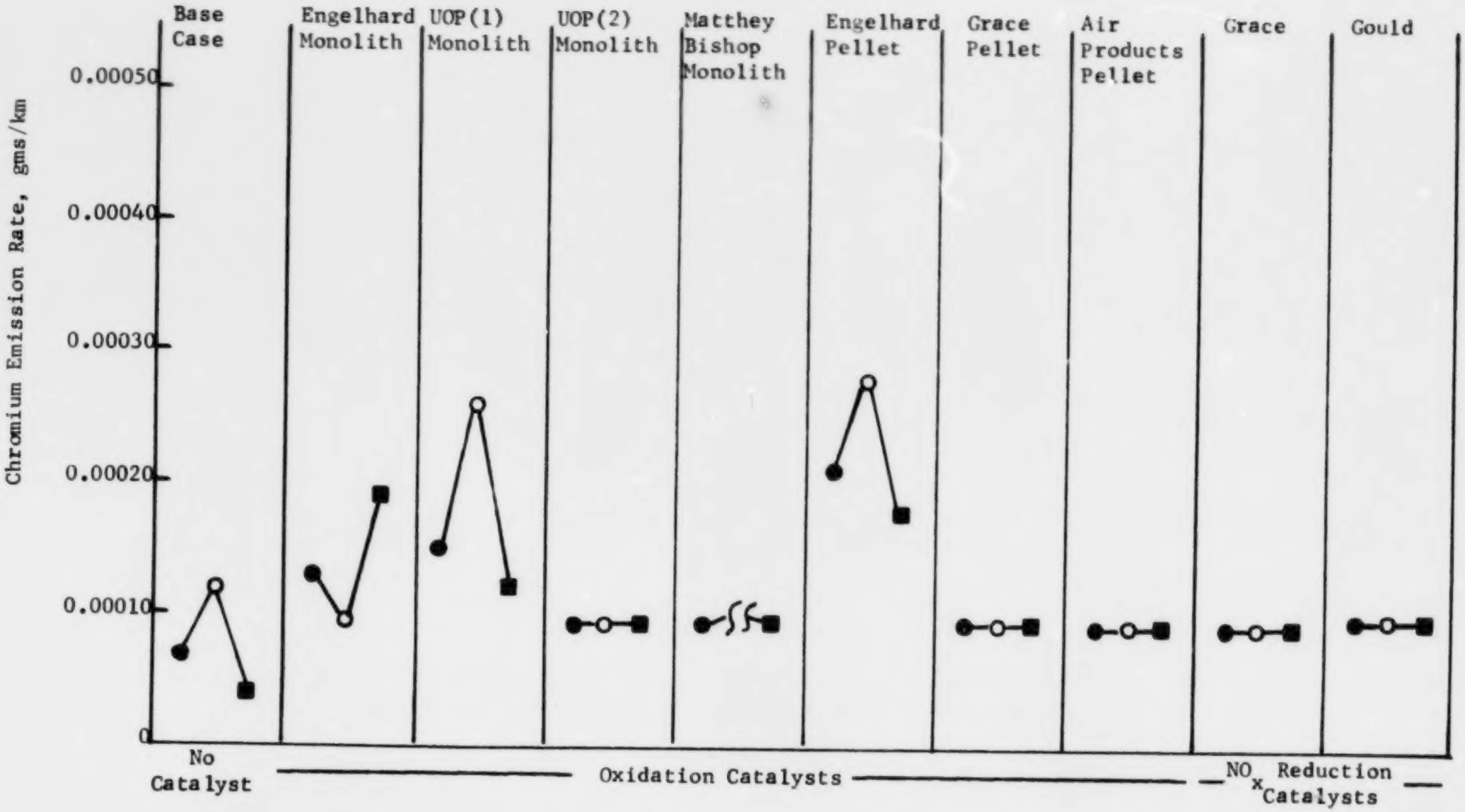


FIGURE IV-51

CHROMIUM EMISSION RATES, gms/km OBTAINED WITH INDICATED CATALYSTS
INITIAL 1975 FTP, ● = 0.019% S, ○ = 0.110% S, ■ = 0.091% S



showed somewhat higher emissions than the base case vehicle, or the vehicle equipped with the other catalyst system.

Elemental analysis on a monolithic Engelhard catalyst carried out at Exxon several years ago showed that chromium was present, so that the Engelhard catalyst systems may be a source for the low chromium emissions observed. These analyses also showed that copper was another elemental constituent such that the copper to chromium ratio averaged about 8 to 1. The ratio of the emitted copper to chromium for the Engelhard monolith was found to range from about 4 to 7.5 in reasonably good agreement with the analysis supporting the hypothesis that these metals are catalyst derived.

No such analytical data is available for the Engelhard pelletized catalyst or the UOP monolithic system. It is probable, however, that in these cases, the catalyst systems are also the sources of the low level chromium emissions.

IV.2.4 Metal Oxide Emission Rates Following Sulfate Storage Conditioning

Metal emission rates were measured on the test sequence carried out following the 3200 km conditioning on the Federal Durability Cycle of the Engelhard pelletized oxidation catalyst-equipped vehicle. The detailed metals emission results are given in Appendix E.

Although sulfate and SO_2 emissions exceeded the theoretical values based on test fuel consumption, the metal emission pattern following storage conditioning was essentially unchanged from that observed after standard conditioning and testing. Table IV-10 shows the comparison of the total metal oxide emission rates for the two sets of conditioning and test sequence.

TABLE IV-10

Comparison of Metal Oxide Emission Rates; Vehicle Equipped with Pelletized Engelhard Oxidation Catalyst, Test Fuel 0.019% S

Test Type	Metal Oxide Emission Rate, gms/km Standard Runs	Metal Oxide Emission Rate, gms/km Storage Runs
1975 FTP	0.0060	0.0070
64 km/hr.	0.0008	0.0004
96 km/hr.	0.0040	0.0004
1975 FTP	0.0090	0.0030

The large difference exhibited at the 96 km/hr. cruise are not believed to be of significance in view of the generally erratic behavior of metallic emissions previously discussed.

IV.3 Organic Exhaust Particulate Emissions

The organic portion of exhaust particulate was to be measured in terms of its carbon content using the semi-microcombustion technique described in Appendix A, Section A.3. Although this technique also could measure the hydrogen content of exhaust particulate, it was not used since it would include the hydrogen present in the particulate as water of hydration. Our earlier work has shown that most of the hydrogen in particulate is present as water of hydration which can be determined separately by the Karl Fisher method discussed in Appendix A, Section A.4.1. Organic hydrogen determined as the small difference between two larger numbers (semi-microcombustion minus Karl Fisher hydrogen) would be an extremely inaccurate number. Consequently, the semi-microcombustion technique was not used to determine organic hydrogen.

The presence of organic nitrogen in exhaust particulate was determined using sensitive spot tests. These tests are discussed in Appendix A, Section A.4.2 and the results in Section IV.3.3. Organic sulfur compounds in exhaust particulate are discussed in Section IV.1.6.

IV.3.1 Carbon Content of Exhaust Particulate

Previous tests had shown that the semi-microcombustion technique may not be sufficiently sensitive to determine organic particulate as carbon, particularly in the case of oxidation catalyst equipped vehicles. The Type A Gelman glass fiber filters used in this program although ostensibly free of organic binder gave somewhat high and variable carbon blanks, which averaged in terms of equivalent emission rates, 0.0014 gms/km for the 1975 FTP, 0.0004 gms/km for the 64 km/hr (40 mph) cruise and 0.0001 gm/km for the 96-112 km/hr (60-70 mph) cruises. As applied to analysis of the carbon content of exhaust particulate laden filters, this method is at best semi-quantitative.

Carbon analysis was performed for the base case runs, and for the 1975 FTP and 64 km/hr cruises for the catalyst equipped vehicle. The detailed results are given in Appendix E. Table IV-11 below compares the organic carbon particulate with the total particulate for the base case vehicle on the 1975 FTP and 64 km/hr test runs on all three fuels. This vehicle was the one which in subsequent tests was equipped with the various catalysts that were screened on this program.

For discussion purposes, the catalysts in Table IV-11 are tabulated with respect to type, not the chronological order in which it was screened.

For the base case vehicle, the carbon content of the exhaust particulate ranged from 25 to 60% of the total particulate.

Carbon particulate from the Engelhard monolith equipped vehicle with several exceptions were lower than the base case vehicle, ranging from essentially zero to at most 11% of the total particulate.

Table IV-11

Comparison of Carbon and Total Particulate Emissions

				Emission Rate, gms/km as	
Run No.	Test Type	% Fuel Sulfur	Catalyst	Carbon	Total Particulate
16	75 FTP	0.019	None	0.002	0.015
18	40(1)	"	"	0.001	0.002
20	75 FTP	"	"	0.005	0.019
21	75 FTP	0.110	"	0.007	0.014
23	40(1)	"	"	0.002	0.004
25	75 FTP	"	"	0.006	0.010
26	75 FTP	0.091	"	0.007	0.014
28	40(1)	"	"	0.003	0.005
30	75 FTP	"	"	0.009	0.014
36	75 FTP	0.019	Engelhard Monolith	0.002	0.031
38	40(1)	"	"	0.000	0.018
40	75 FTP	"	"	0.000	0.043
41	75 FTP	0.110	"	0.002	0.169
43	40(1)	"	"	0.005	0.262
45	75 FTP	"	"	0.014	0.150
46	75 FTP	0.091	"	0.014	0.226
48	40(1)	"	"	0.005	0.192
50	75 FTP	"	"	0.015	0.131
66	75 FTP	0.019	UOP(1)	0.019	0.029
68	40(1)	"	"	0.005	0.037
70	75 FTP	"	"	0.015	0.035
71	75 FTP	0.110	"	0.015	0.104
73	40(1)	"	"	0.006	0.490
75	75 FTP	"	"	0.012	0.090
76	75 FTP	0.091	"	0.014	0.134
80	75 FTP	"	"	0.014	0.042
141	75 FTP	0.019	UOP(2)	0.012	0.023
143	40(1)	"	"	0.000	0.025
145	75 FTP	"	"	0.001	0.014
146	75 FTP	0.110	"	0.001	0.070
148	40(1)	"	"	0.002	0.363
150	75 FTP	"	"	0.001	0.151
151	75 FTP	0.091	"	0.001	0.173
153	40(1)	"	"	0.006	0.356
155	75 FTP	"	"	0.005	0.134
81	75 FTP	0.019	Matthey Bishop	0.014	0.028
83	40(1)	"	" "	0.004	0.014
85	75 FTP	"	" "	0.015	0.021
86	75 FTP	0.110	" "	0.015	0.086
88	40(1)	"	" "	0.004	0.118
90	75 FTP	"	" "	0.014	0.050
91	75 FTP	0.091	" "	0.014	0.069
93	40(1)	"	" "	0.004	0.087
95	75 FTP	"	" "	0.015	0.040

Table IV-11 (Cont'd.)

Run No.	Test Type	% Fuel Sulfur	Catalyst	Emission Rate, gms/km as Carbon	Emission Rate, gms/km as Total Particulate
55	75 FTP	0.019	Engelhard Pellet	0.015	0.036
60	75 FTP	0.110	"	0.015	0.083
61	75 FTP	0.091	"	0.015	0.062
63	40(1)	"	"	0.015	0.201
65	75 FTP	"	"	0.014	0.064
126	75 FTP	0.019	Grace Pellet	0.013	0.044
128	40(1)	"	" "	0.004	0.016
130	75 FTP	"	" "	0.012	0.026
131	75 FTP	0.110	" "	0.014	0.027
133	40(1)	"	" "	0.005	0.117
135	75 FTP	"	" "	0.017	0.065
136	75 FTP	0.091	" "	0.013	0.066
138	40(1)	"	" "	0.004	0.140
140	75 FTP	"	" "	0.011	0.051
156	75 FTP	0.019	Air Products Pellet	0.002	0.034
158	40(1)	"	"	0.001	0.020
160	75 FTP	"	"	0.000	0.010
161	75 FTP	0.110	"	0.002	0.051
163	40(1)	"	"	0.003	0.149
165	75 FTP	"	"	0.002	0.106
166	75 FTP	0.091	"	0.002	0.043
168	40(1)	"	"	0.004	0.099
170	75 FTP	"	"	0.001	0.123
96	75 FTP	0.019	Grace NO_x Reduction	0.000	0.007
98	40(1)	"	"	0.000	0.005
100	75 FTP	"	"	0.000	0.017
101	75 FTP	0.110	"	0.000	0.016
103	40(1)	"	"	0.000	0.133
105	75 FTP	"	"	0.000	0.019
106	75 FTP	0.091	"	0.002	0.020
108	40(1)	"	"	0.004	0.118
110	75 FTP	"	"	0.016	0.041
113	40(1)	0.019	Gould NO_x Reduction	0.004	0.005
115	75 FTP	"	"	0.006	0.013
116	75 FTP	0.110	"	0.014	0.025
121	75 FTP	0.091	"	0.016	0.031
123	40(1)	"	"	0.004	0.089
125	75 FTP	"	"	0.018	0.019

There are differences not understood between the two UOP oxidation catalysts. The UOP(1) system shows a carbon emission rate generally higher than the base case vehicle, whereas the UOP(2) system shows with one exception lower carbon emissions that the base case vehicle. A suggested possible explanation is that the emission pattern of carbonaceous exhaust particulate may be similar to the metal oxide emission pattern. Thus, a portion of the carbonaceous material collected during the UOP(1) runs may have been re-entrained carbon deposits and not freshly made carbonaceous material. The base case tests regarding carbon emissions may be atypical in that the emissions were coursing through a clean exhaust system. Thus, an appreciable fraction of the carbonaceous particulate matter produced in the base case runs may have deposited on the walls of the exhaust pipe and re-emitted in subsequent test runs. Although both catalysts met the stringent CO and hydrocarbon standards, the UOP(1) catalyst vehicle consistently showed higher CO emissions. This may also be a factor involved in the different levels of carbonaceous particulate by the two UOP catalyst systems.

The carbon emission rates on the FTP's for the Matthey Bishop catalyst equipped vehicle are consistently higher than the base case vehicle whereas the emission rates under cruise conditions are generally lower. The higher carbonaceous particulate emission rates on the FTP may not only be due to the cold starts, but also to the effect of vehicle aging in terms of carbonaceous deposits, which may be released and re-entrained during the acceleration and deceleration portions of the driving cycle.

A similar carbon emission pattern to the Matthey Bishop system was observed with the Engelhard and Grace pelletized catalyst equipped vehicle. Presumably these patterns are due to similar but undetermined factors operating in each case.

The carbonaceous exhaust emission rates with the Air Products catalyst equipped vehicle are the lowest that have been obtained of all the oxidation catalysts that have been screened.

The lowest carbon emission rates regardless of the catalyst type screened were obtained with the Grace NO_x reduction catalyst. A possible explanation is that the order of catalyst testing may have a greater effect on transient carbonaceous emissions than the catalyst itself.

The particulate emissions from the Gould NO_x reduction catalyst equipped vehicle are predominantly carbonaceous with the exception of a 64 km/hr cruise, run 123 Table IV-11. The operating conditions in that run were sufficiently lean to produce sulfuric acid at an emission rate of 0.034 gms/km. If it is assumed that the H_2SO_4 particulate is about a 50 wt.% aqueous solution, then the particulate emission rate for run 123 excluding H_2SO_4 and bound water is 0.021 gms/km. The carbon particulate now constitutes 25% of the residual particulate.

In general, the interpretation of the organic particulate emissions from the catalyst equipped vehicle is difficult since the test sequence was designed for a gross characterization of exhaust particulate, rather than for the elucidation of the detailed mechanism of organic particulate formation and emission. For example, there is no way to assess the effects if any of the test sequence on the resultant organic particulate emission rates. In addition, the screening program was not designed to separate cold start effects from cycling effects, both of which could markedly influence organic particulate emission rates.

IV.3.2 Organic Nitrogenous Particulate

Chemical spot tests were carried out on particulate samples generated from the 1975 FTP and 64 km/hr (40 mph) test runs for nitrogenous organic material. As in the case of non-sulfate sulfur particulate analysis, the samples analyzed included those from runs on the unequipped vehicle, and when the vehicle was equipped with the various catalysts screened on the test program.

Low levels of nitrogenous particulate matter should be readily detectable due to the extreme sensitivity of the tests. Negative results would establish the maximum emission rate possible. This maximum rate is based on the test sensitivity, the mileage accumulated on the particular test run, and the fraction of the filter area selected for testing. The spot tests used are listed in Feigl(22), and are discussed in detail in Appendix A, Section A.4.2.

Table IV-12 below shows which nitrogenous organic compounds were tested for, and the maximum emission rates for the 1975 FTP and 64 km/hr cruise based on negative results.

Table IV-12

ESTIMATED AVERAGE MAXIMUM EMISSION RATES AS DETERMINED BY DETECTION LIMITS

	gms/km, on Indicated Test	
Compound Type	1975 FTP	64 km/hr Cruise
Organic Nitrogen	1×10^{-5}	2.5×10^{-6}
Compounds with Nitrogen-oxygen bonds	2×10^{-4}	5×10^{-5}
Aliphatic and Aromatic Nitro Compounds	3×10^{-4}	7.5×10^{-5}
Primary Aliphatic Nitro Compounds	2×10^{-4}	5×10^{-5}
Aromatic Nitro Compounds	6×10^{-4}	1.5×10^{-4}
Nitrates, Nitrites	3×10^{-4}	8×10^{-6}
Aliphatic and Aromatic Nitriles	4.4×10^{-3}	1.1×10^{-3}
Aliphatic Nitriles	4×10^{-3}	1×10^{-3}

The selection of the compound types in the above table as possible exhaust particulate components is based on chemical species known to be present in auto exhaust which could function as precursors or as reactants involved in their production. The basis of this selection is discussed in Appendix D. Two of the three test fuels contained nitrogenous additives such that the nitrogen content of the fuel due to these additives is only about 3 ppm by weight.

All tests for the nitrogenous compounds listed in Table IV-12 were negative. No nitrate other than normal filter background (∿0.1 μgm/cm^2) was detected. There are two tests for nitrate which have detection limits of 0.5 and 0.07 μgms of nitrate, respectively. The less sensitive test was always negative, the more sensitive one always positive when a 0.39 cm^2 section of filter was tested. The background nitrate level corresponds to an emission rate for the 1975 FTP of about 3×10^{-5} gms/km, the detection limit of the more sensitive test for nitrate. The nitrate emission rate corresponding to the detection limit of the less sensitive test which was always negative is 2×10^{-4} gms/km. Thus, it may be inferred from the above discussion that the detected nitrate is the background nitrate on the filter.

It is not surprising that none of the nitrogen containing compound types were found in exhaust particulate. The major reason is that there is not enough of the nitrogenous additives present in the fuel to produce sufficient quantities of exhaust nitrogen compounds to have a two-phase (vapor plus liquid) co-existence. Only the liquid form would be collected as particulate matter, and it cannot exist as liquid under the test conditions. This is discussed in detail in Appendix D which also includes a sample calculation for demonstration.

Only high molecular weight nitrogenous organic compounds could exist as particulate matter under vehicle test conditions, and it is unlikely that these would survive the combustion process intact. Consequently, the only mechanism whereby organic nitrogen compounds could be present as exhaust particulate would be if they were strongly absorbed by exhaust particulate. The failure to detect these compounds indicates that absorption of appreciable amounts of these compounds on exhaust particulate does not occur.

IV.4 Size Distribution of Exhaust Particulate

Size distribution of the exhaust particulate was determined using the modified Andersen Impactor in parallel with the other sampling probes. The results obtained with the impactor were considered valid only if the normalized total particulate emission rates obtained with the impactor (sum of weight gains of the impactor stages and final filter) agreed with the total filter particulate emission rates. Acceptable internal agreement between the impactor measured emission rates and total filter measured total particulate emission rates were obtained in about 20% of the runs. It is believed that the major source of the discrepancy was due to improper placement of the final filter in the impactor. This filter holder could not be sealed in the filter holder, so that large portions of aerosol could be lost by improper placement. The rapid disassembly and reassembly of the impactor that was required on the days when 4 tests were conducted on the vehicle may have contributed to many instances in which the final filter was misaligned. Periodic checks showed that variable flow rates and visible leaks around the collection surface were not sources of error.

The nature of the program was such that considerable time lags occurred between sample generation and weighing of the impactor plates. Consequently, the extent of the discrepancy was not noted till late in the program. However, it should be noted that those cases where agreement was obtained included FTP's. Table IV-11 shows the comparison of the total particulate emission rates obtained with the impactor and the total filter. The asterisk marked runs denote those in which the agreement between the impactor and the total filter were sufficiently close so that the impactor results could be considered valid. Figures IV- 52 to IV- 67 show the log normal distribution plots for the asterisk marked runs.

IV.4.1 Particle Size Distributions, Base Case Vehicle

For the base case vehicle runs, Figures IV- 52 to IV- 56 the predominant fraction of the particles are under 2 microns. For the FTP's shown in Figures IV- 52 and IV- 55, the cumulative % mass of particles less than 2 microns ranged from 91.5 to 95%. For the hot start cruises, the cumulative % mass of particles less than 2 microns, Figures IV- 53, IV- 54 and IV- 55, the cumulative % mass shifted to a range of 96 to 98.6%. The major difference between the cold start cyclic testing and the hot start cruises is most likely the result of greater production of organic particulate during the cold start. A comparison of the organic emissions (as carbon) Section IV.3.1, shows that the hot start cruises for the base case vehicle consistently produces lower levels of these emissions.

IV.4.2 Particle Size Distributions, Oxidation Catalyst Equipped Vehicle

With oxidation catalyst equipped vehicles, the cumulative % mass of particles less than 2 microns shifted from 98.2 to 99.7%, Figures IV-57 to IV-61. This means that exhaust particulate from oxidation catalyst equipped vehicles is smaller than that emitted from a conventional vehicle. Virtually none of the particles are in the size range above 2 microns. There is not sufficient data to show trends in operating conditions or fuel sulfur levels. However, in the cases with the oxidation catalyst equipped vehicle, the sulfuric acid aerosol accounted for about 50% of the total particulate. Thus, taking into account the bound water associated with the acid, the particulate is predominantly sulfuric acid aerosol.

Figure IV-52
Size Distribution of Total Particulate,
Base Case Vehicle, 1975 FTP, Run No. 6

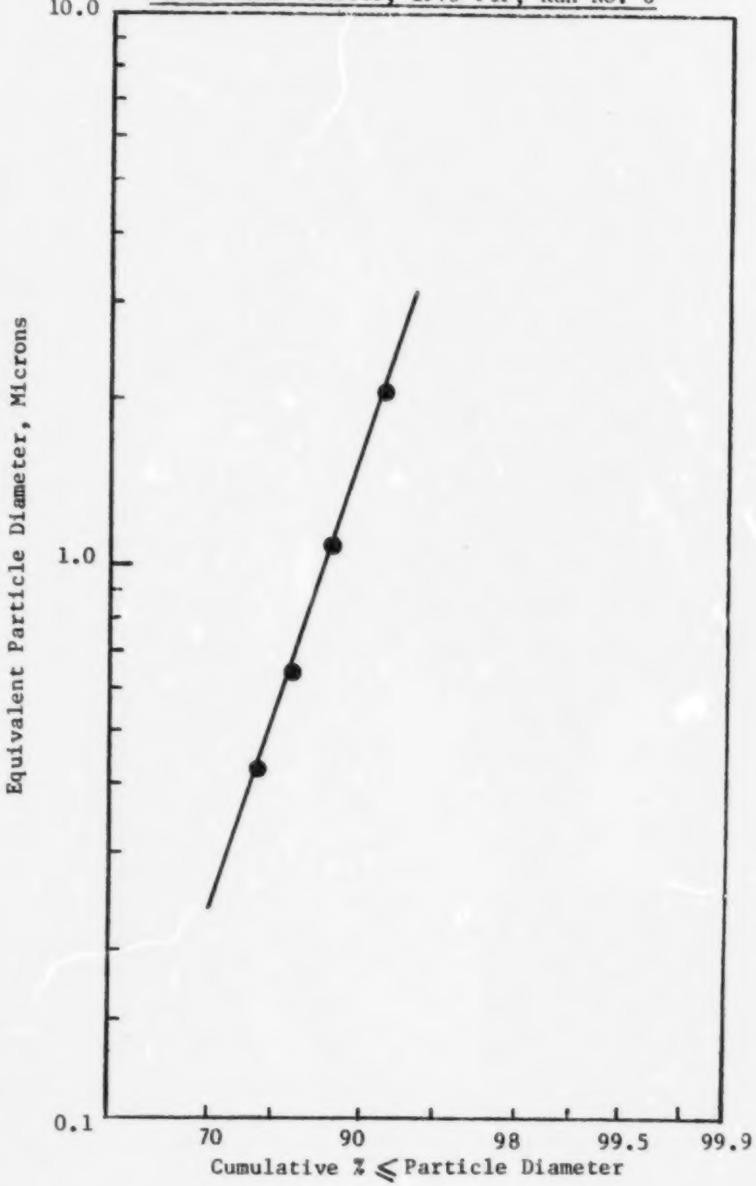


Figure IV-53
Size Distribution of Total Particulate,
Base Case Vehicle, 113 km/hr Cruise, Run No. 9

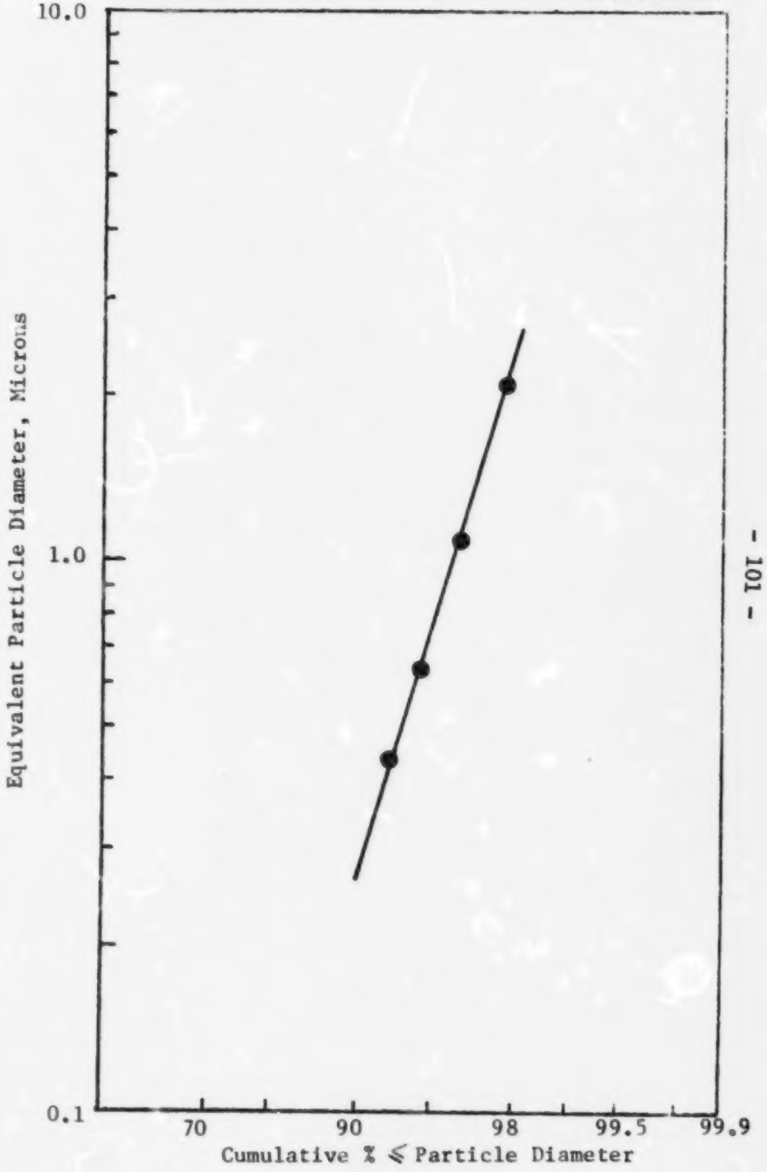


Figure IV-54
Size Distribution of Total Particulate,
Base Case Vehicle 113 km/hr Cruise, Run No. 14

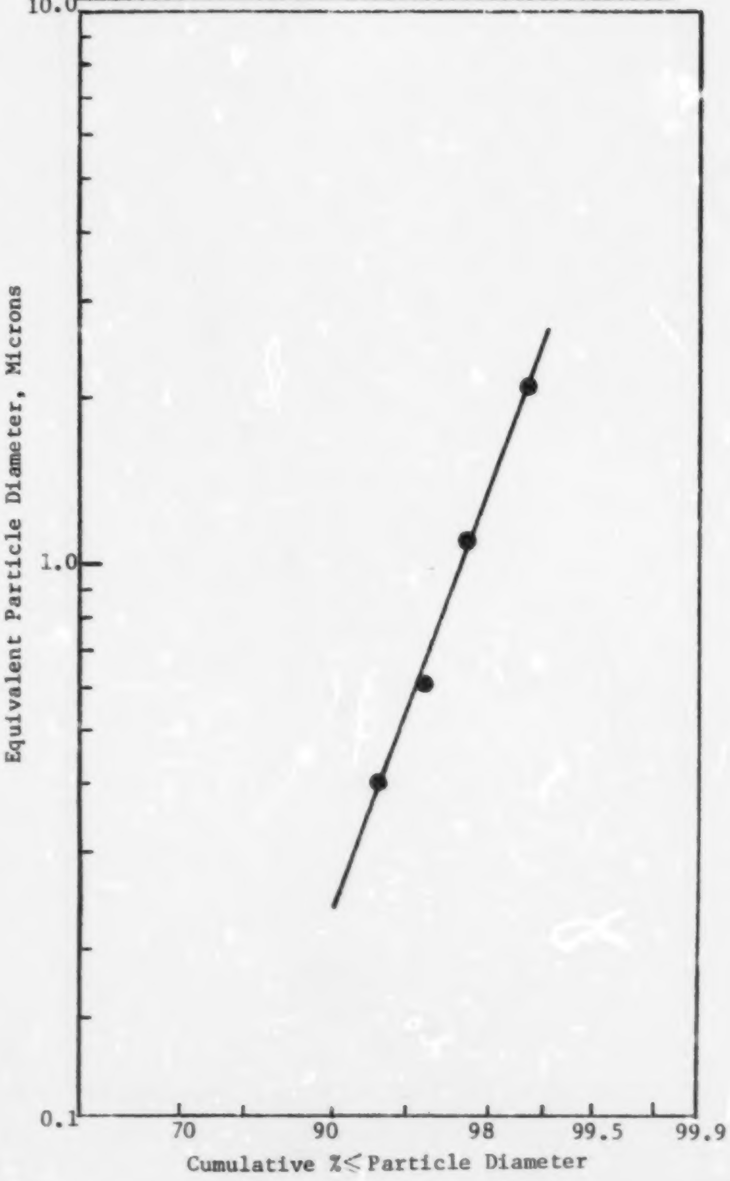


Figure IV-55
Size Distribution of Total Particulate,
Base Case Vehicle, 1975 FTP Run No. 15

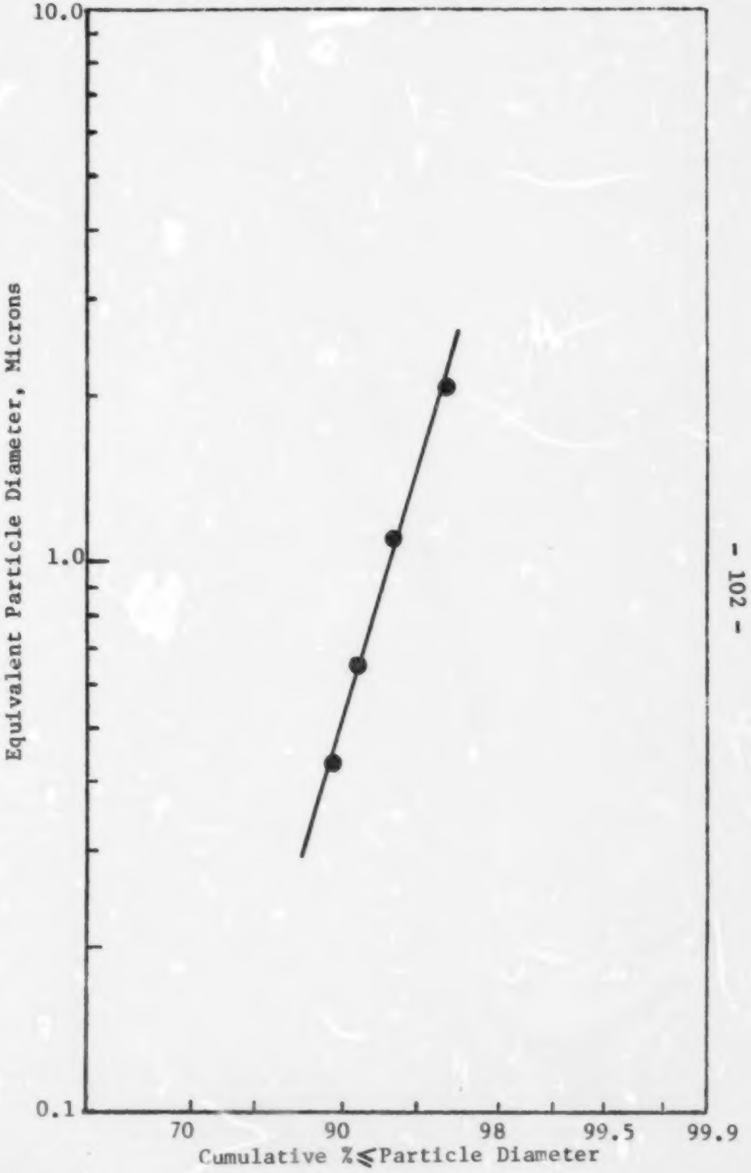


Figure IV-56

Size Distribution of Total Particulate,

Base Case Vehicle, 64 km/hr Cruise, Run No. 29

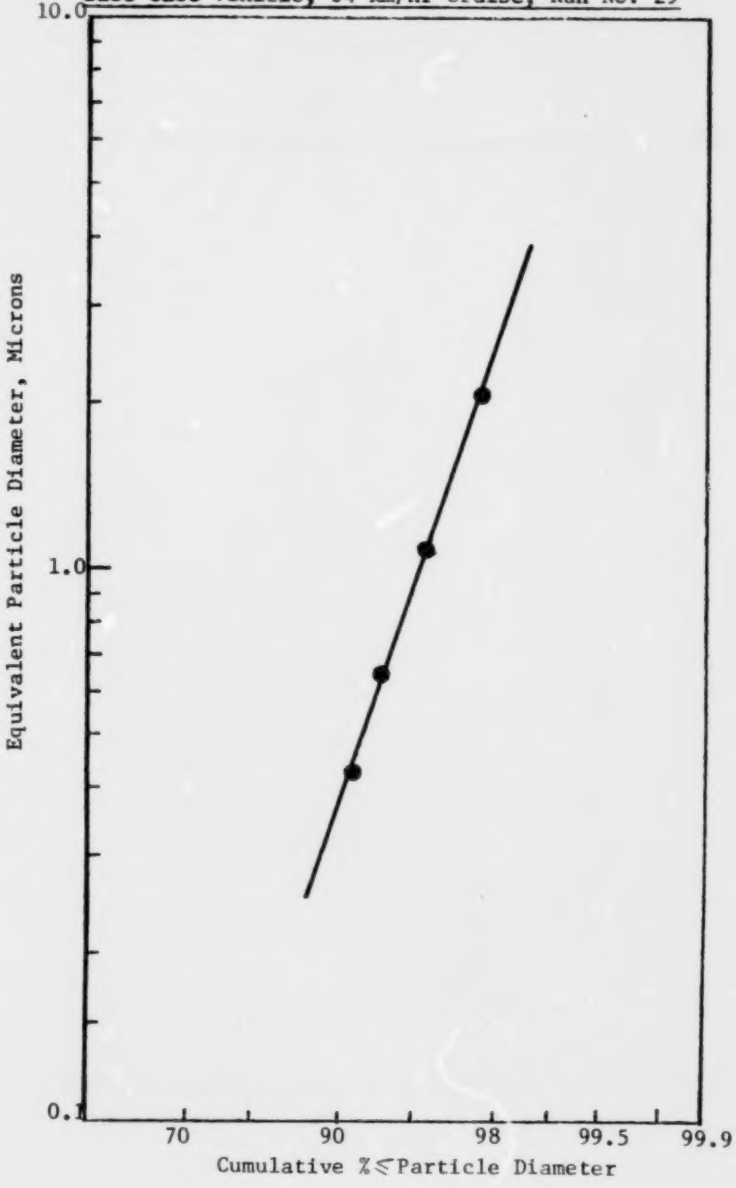


Figure IV-57

Size Distribution of Total Particulate, Matthey Bishop

Catalyst-Equipped Vehicle, 64 km/hr Cruise, Run No. 88

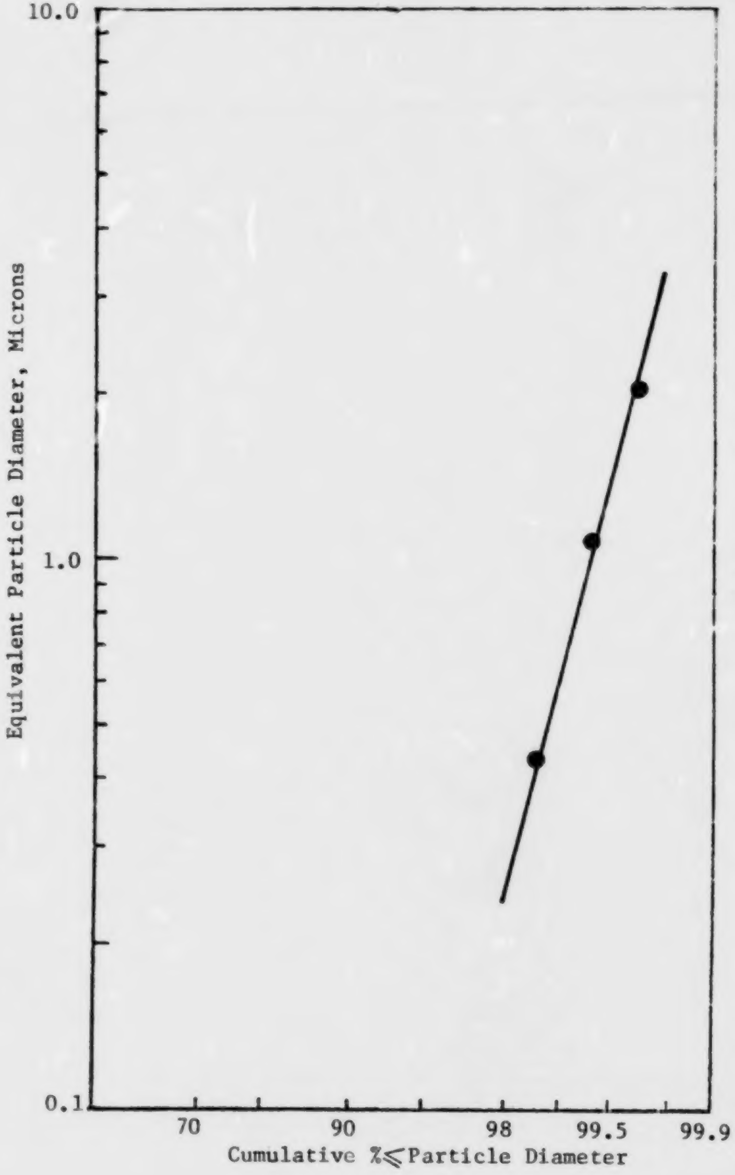


Figure IV-58
Size Distribution of Total Particulate, Grace Pelletized
Catalyst-Equipped Vehicle, 64 km/hr Cruise, Run No. 133

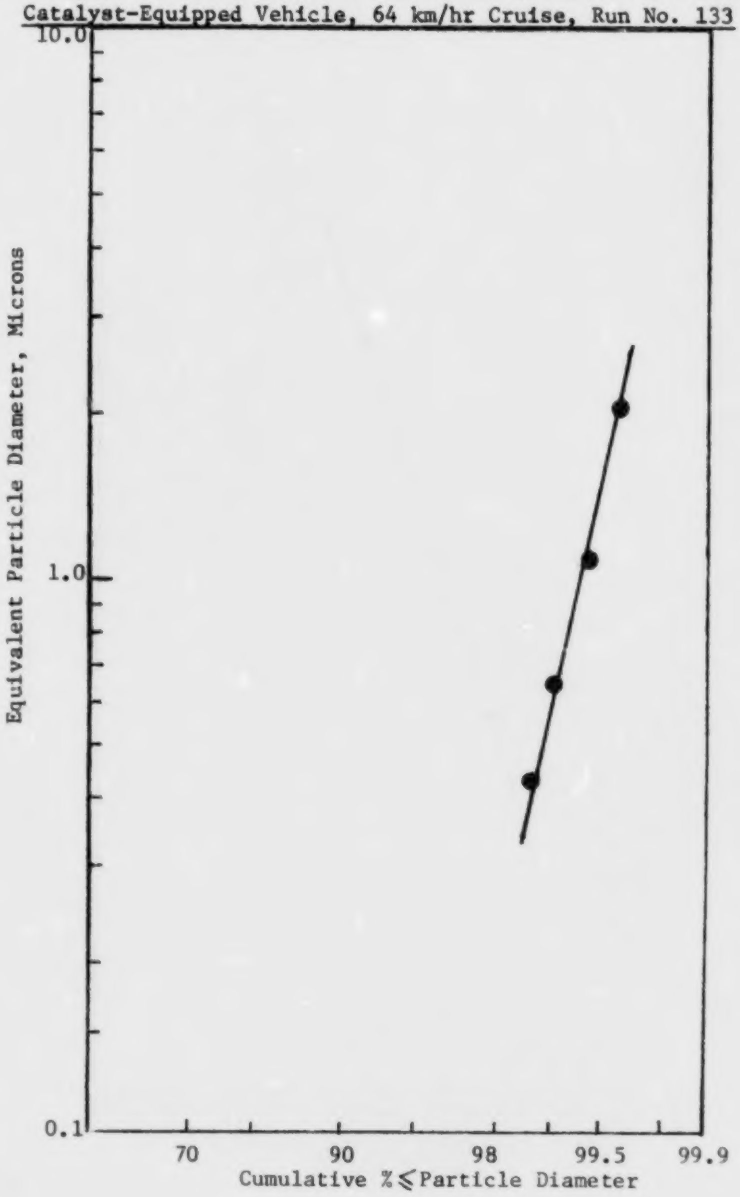


Figure IV-59
Size Distribution of Total Particulate, Grace Pelletized
Catalyst-Equipped Vehicle, 64 km/hr Cruise, Run. No. 138

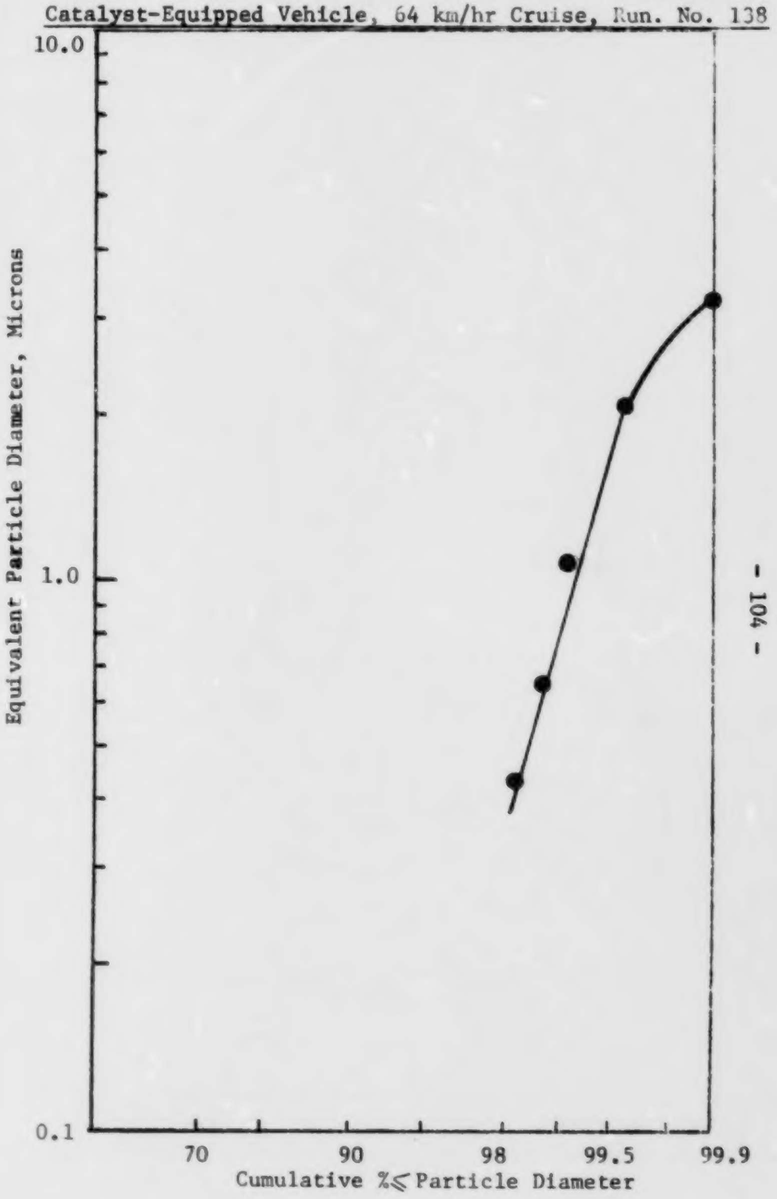


Figure IV-60

Size Distribution of Total Particulate, Air Products Pelletized Catalyst Equipped Vehicle 1975 FTP Run No. 160

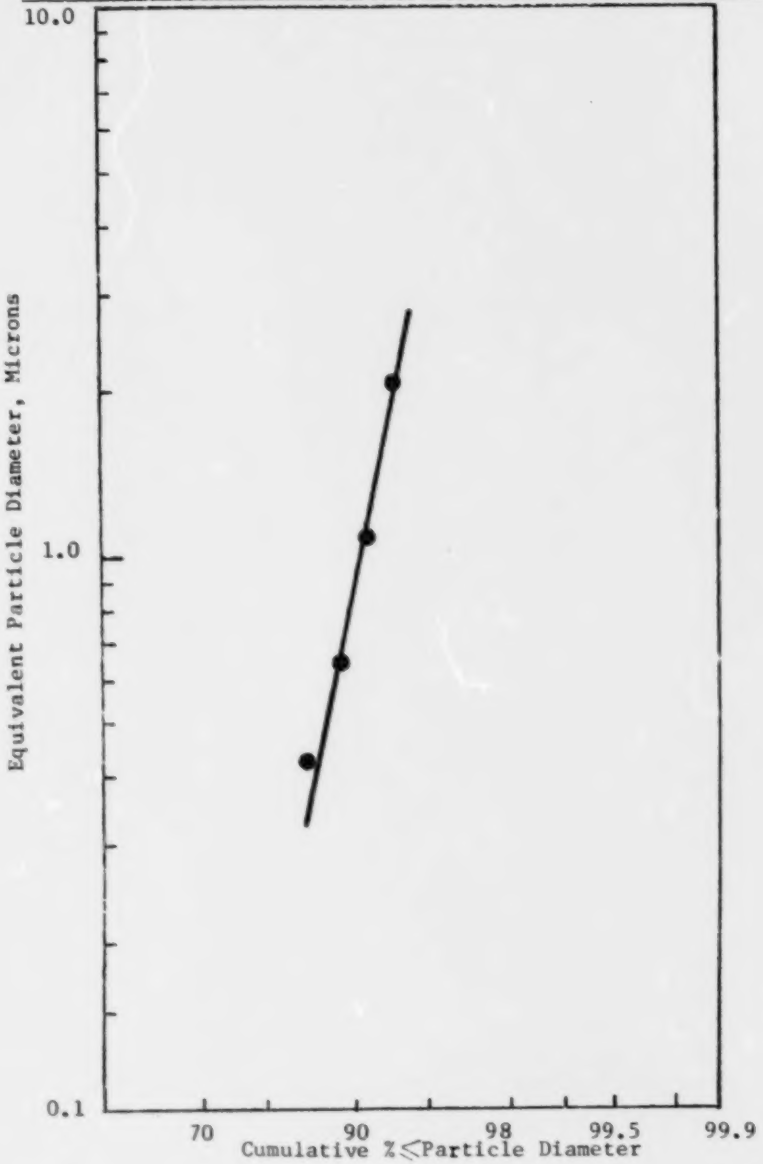


Figure IV-61

Size Distribution of Total Particulate, Air Products Pelletized Catalyst Equipped Vehicle 1975 FTP Run No. 166

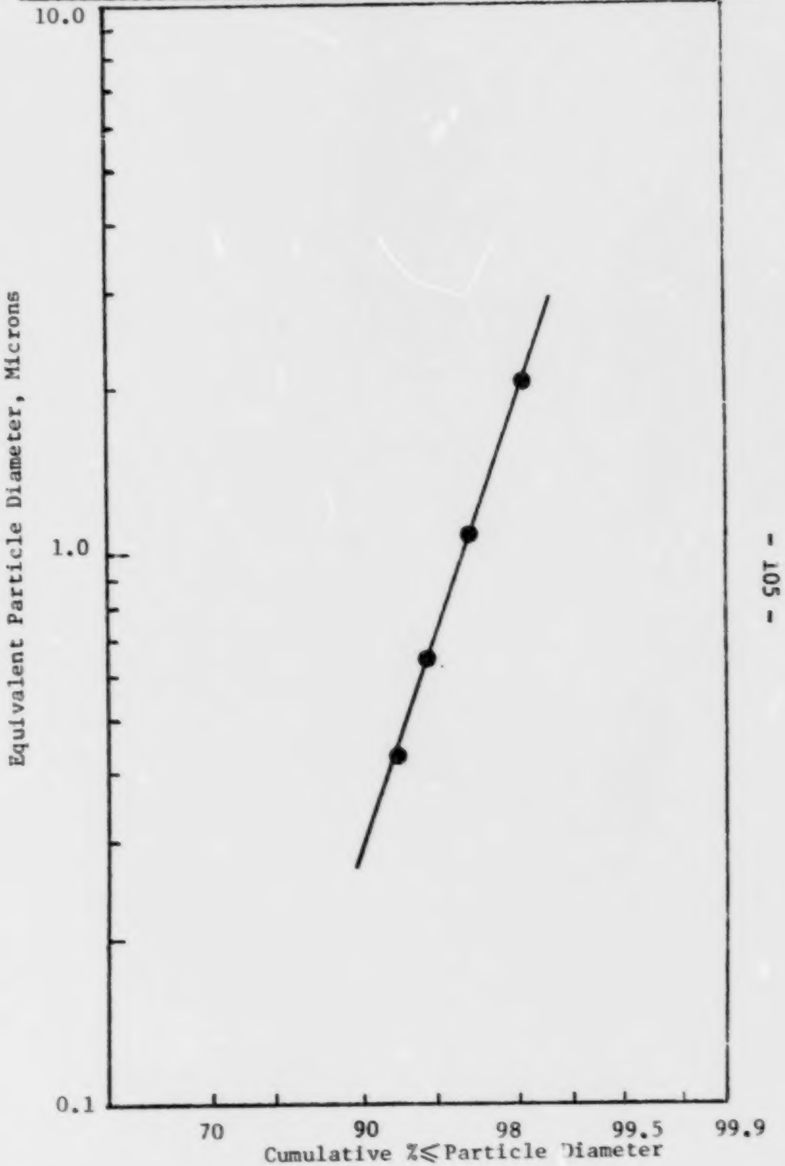


Figure IV-62
Size Distribution of Total Particulate, Grace Reduction Catalyst Equipped Vehicle, 1975 FTP Run No. 96

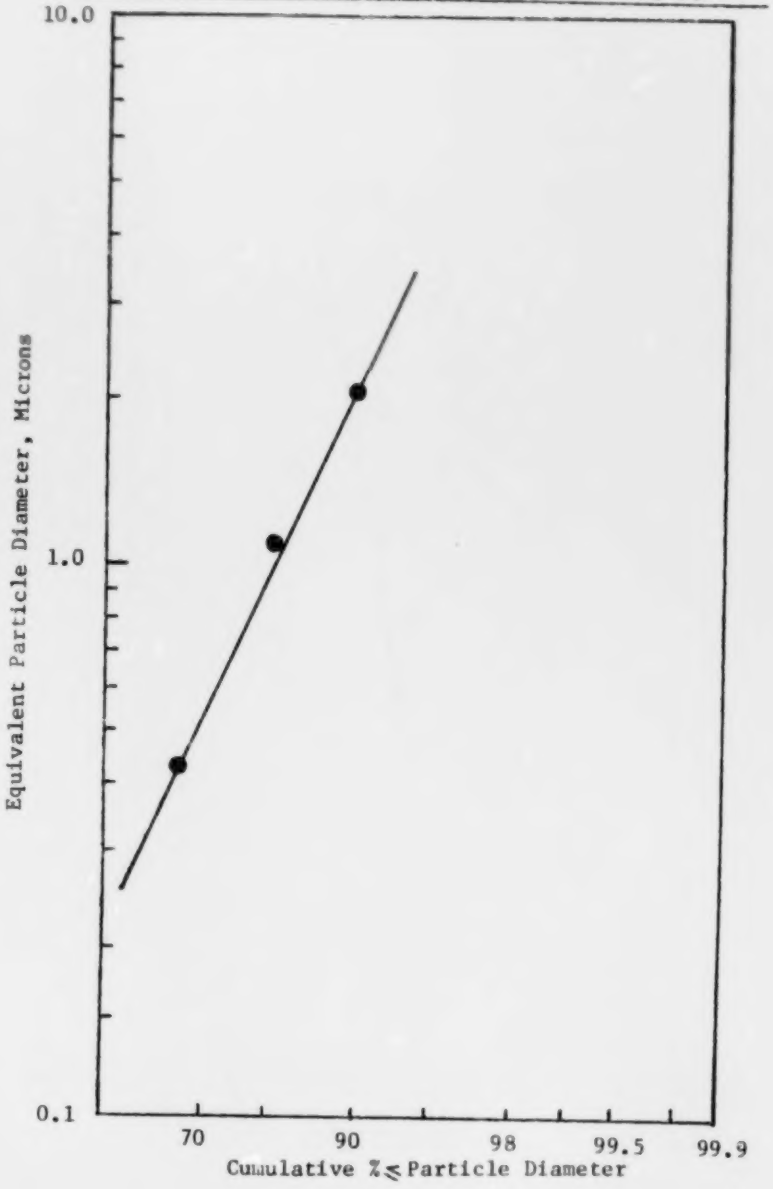


Figure IV-63
Size Distribution of Total Particulate, Grace Reduction Catalyst Equipped Vehicle, 1975 FTP Run No. 101

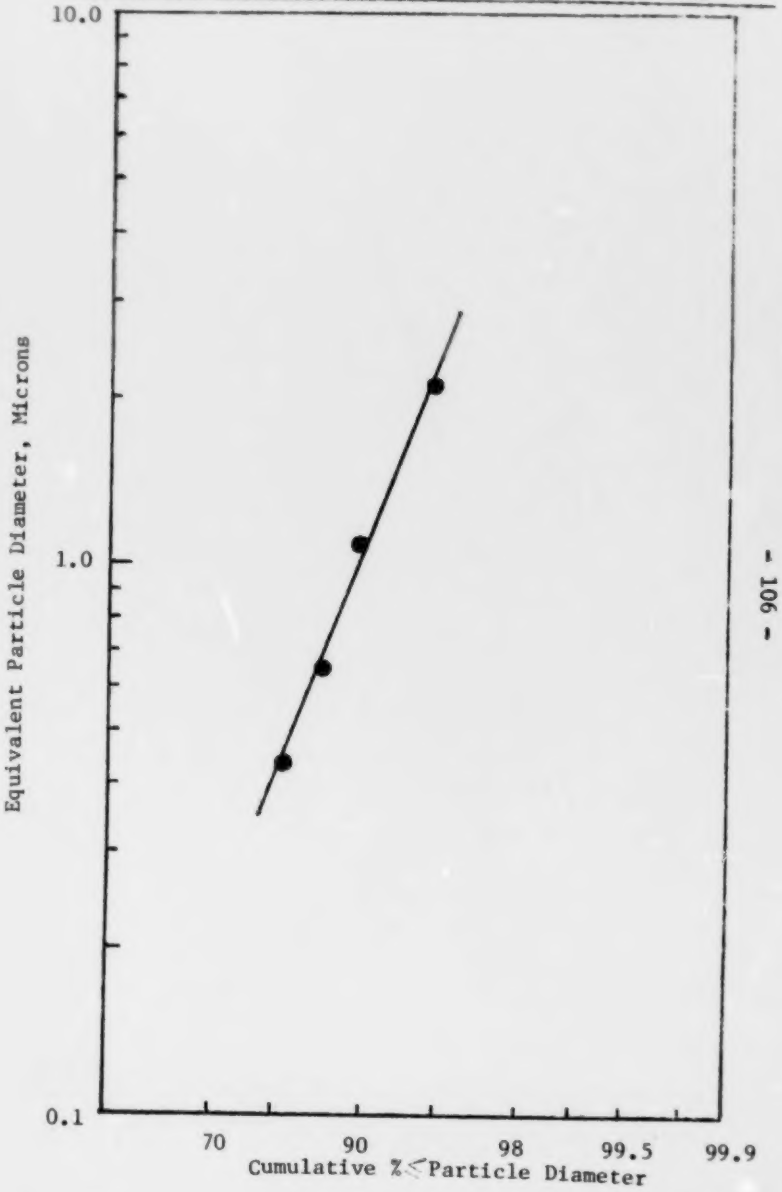


Figure IV-64
Size Distribution of Total Particulate, Gould Reduction
Catalyst-Equipped Vehicle, 64 km/hr Cruise, Run No. 113

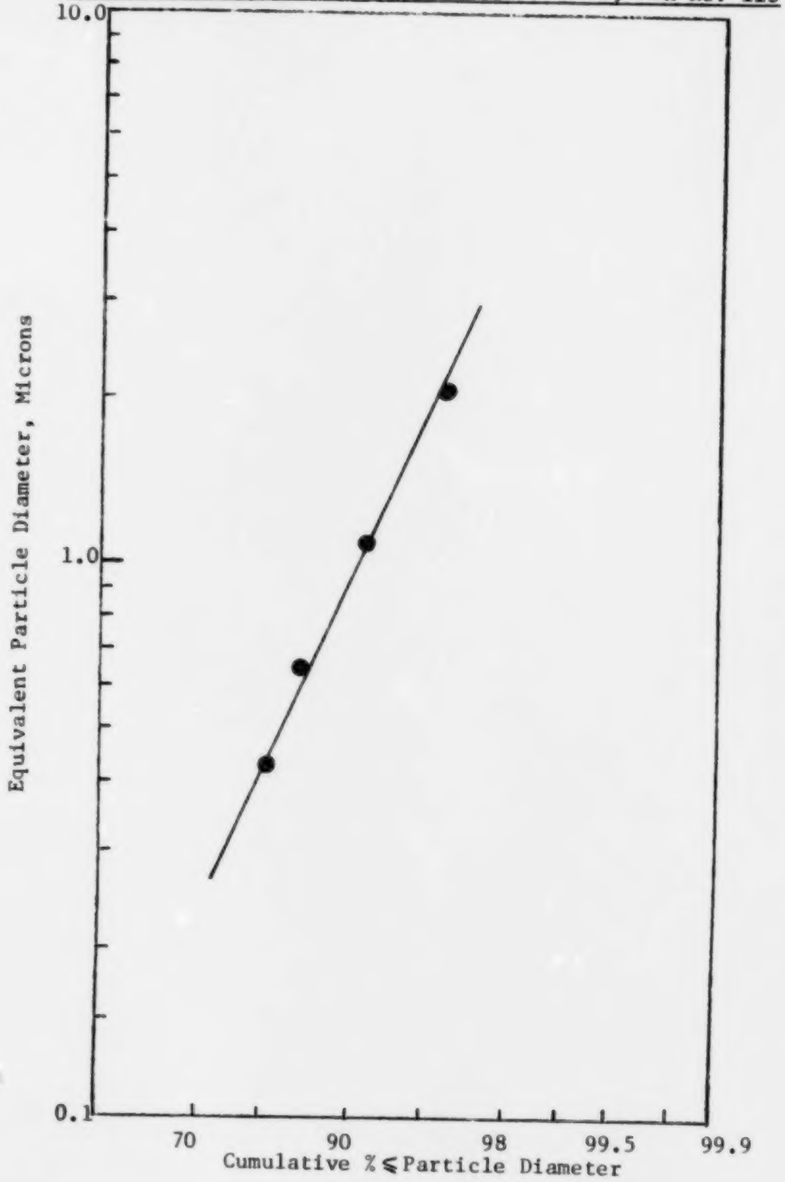


Figure IV-65
Size Distribution of Total Particulate, Gould Reduction
Catalyst-Equipped Vehicle, 1975 FTP, Run No. 120

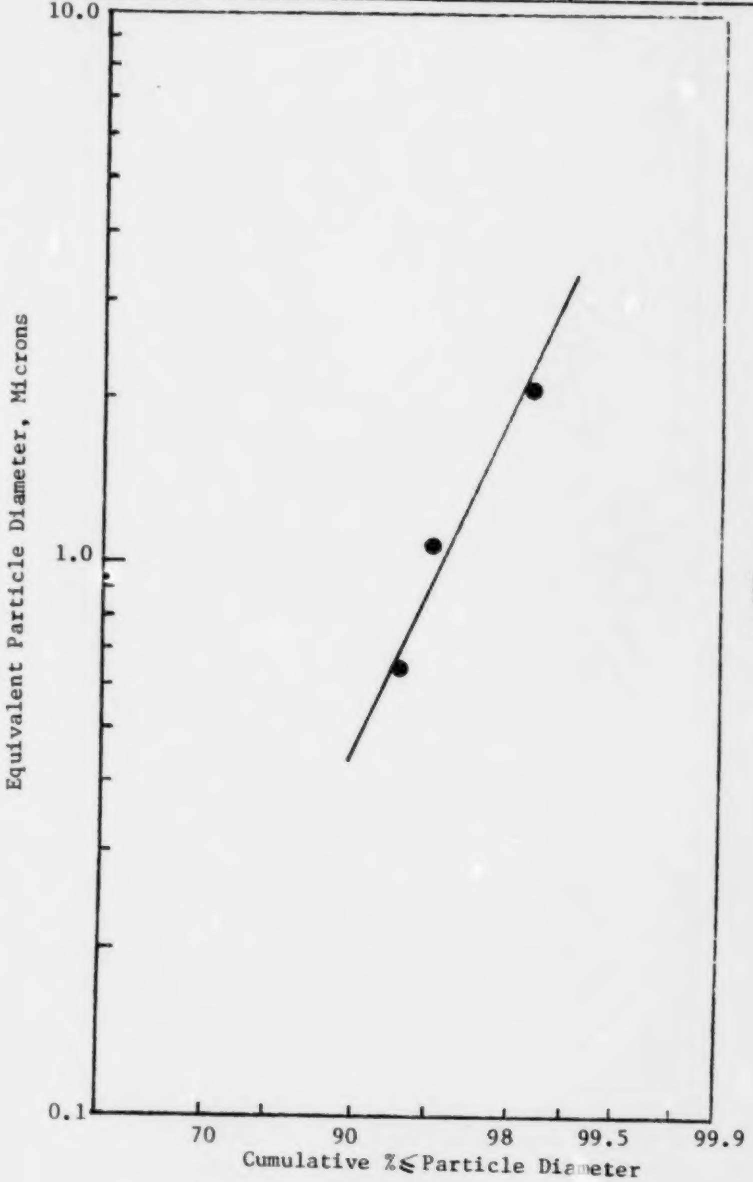


Figure IV-66
Size Distribution of Total Particulate, Grace Reduction
Catalyst Equipped Vehicle, 64 km/hr Cruise Run No. 103

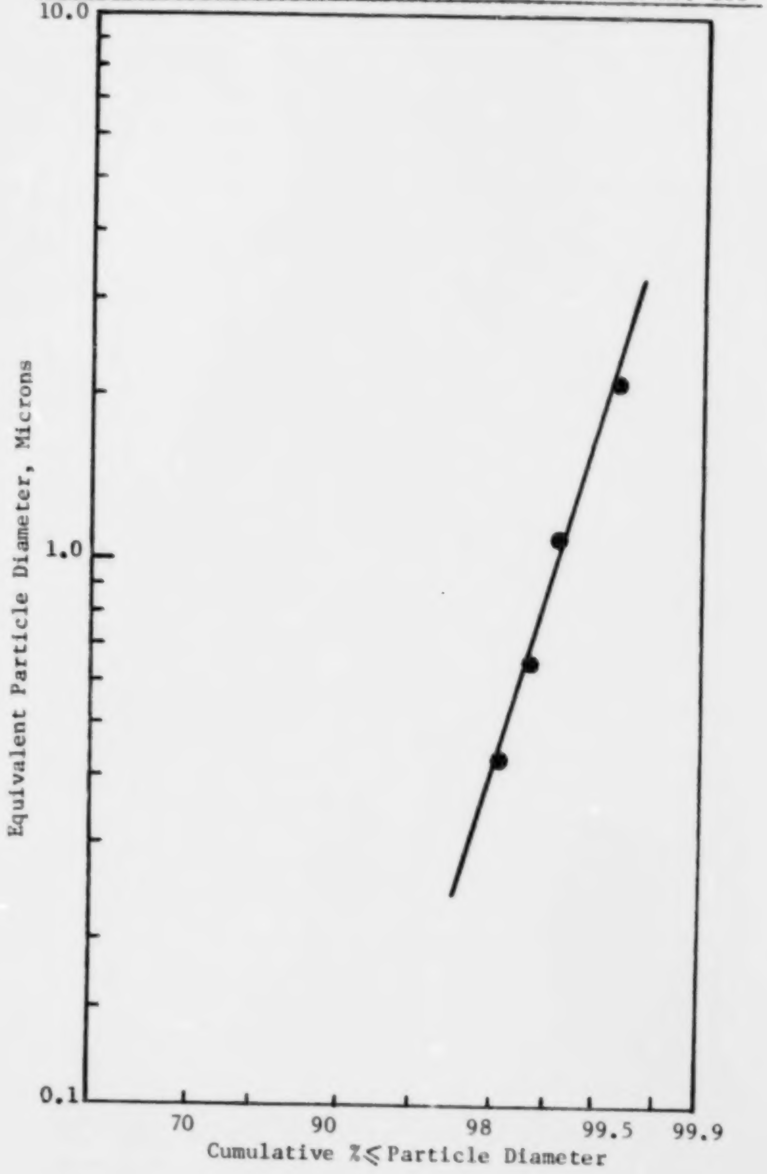


Figure IV-67
Size Distribution of Total Particulate, Gould Reduction
Catalyst-Equipped Vehicle, 1975 FTP, Run No. 125

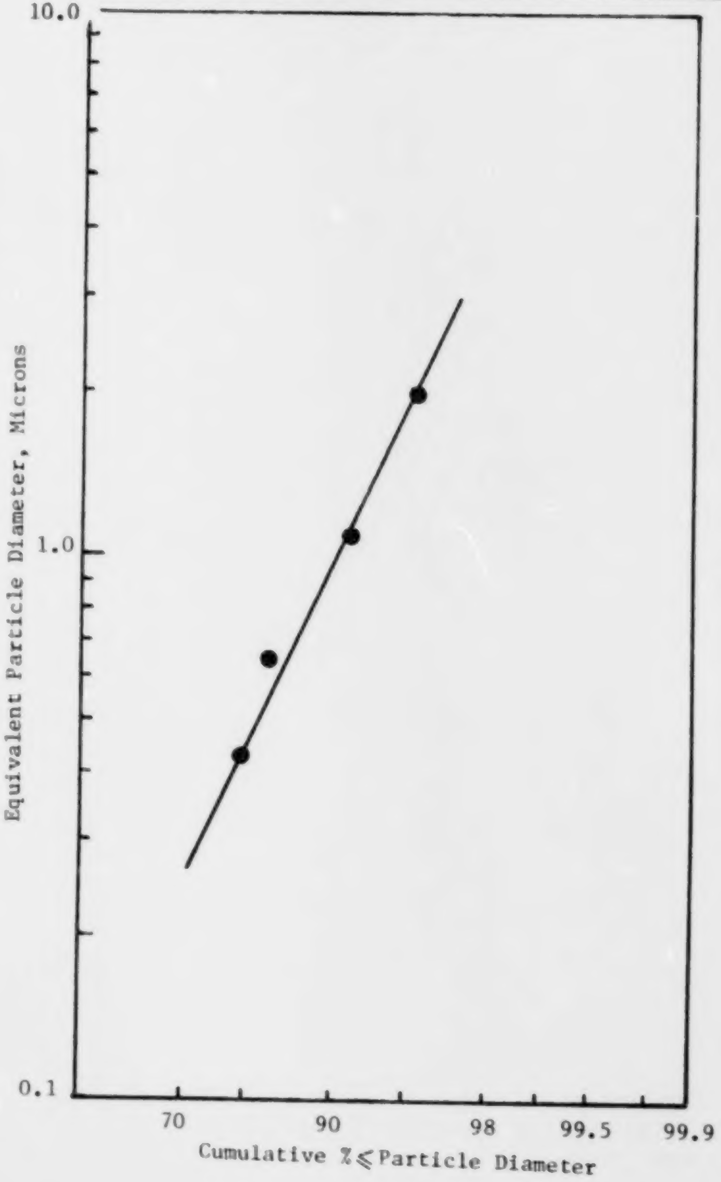
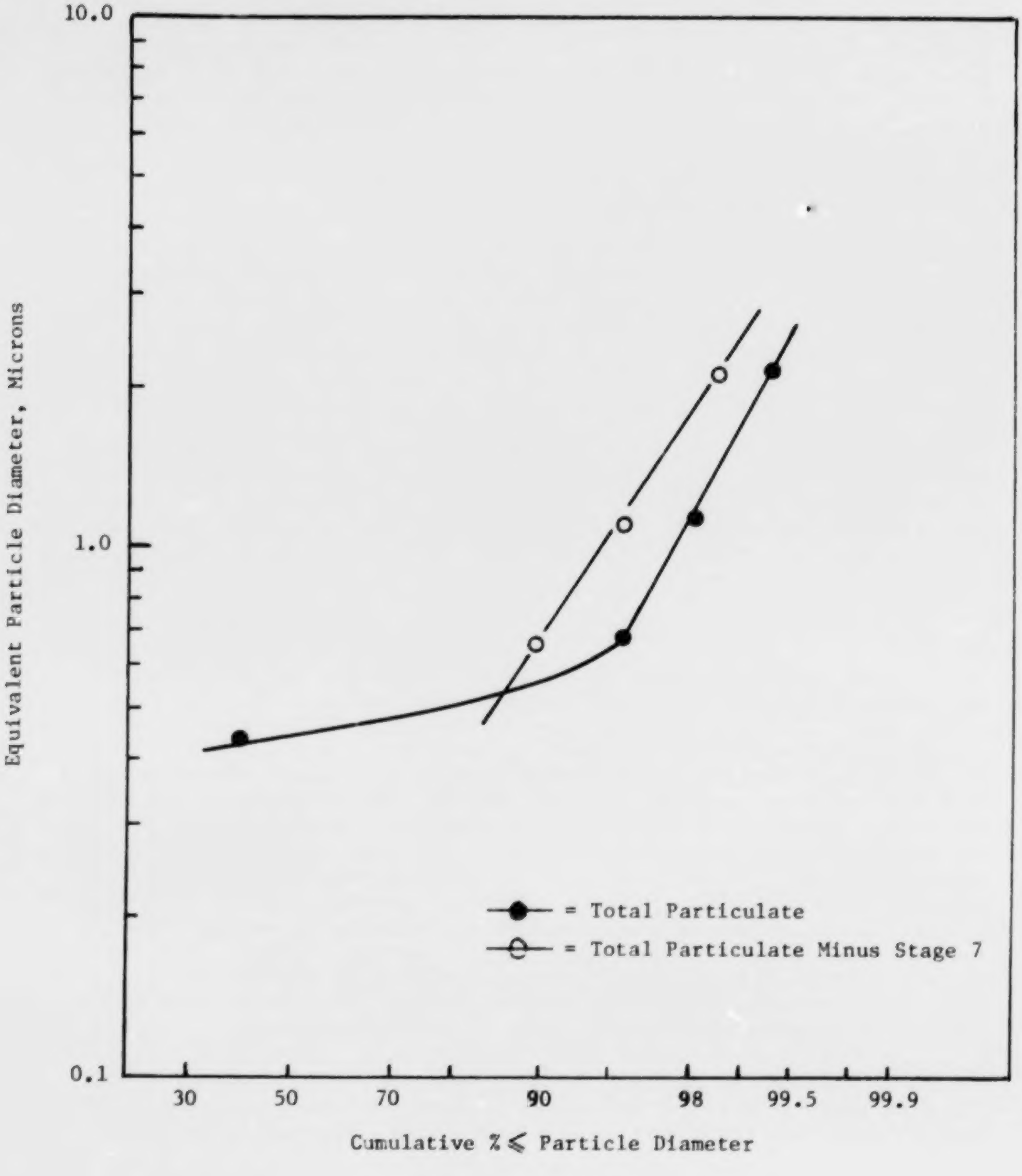


Figure IV-68

Size Distribution of Total Particulate, Engelhard Pelletized Catalyst Equipped Vehicle, Second 1975 FTP After Sulfate Storage Conditioning, Run No. 175



In one case with an Air Products catalyst Run No. 160, Figure IV-60, the cumulative % mass of particles less than 2 microns was 93%, atypical for oxidation catalyst equipped vehicles. This run was an FTP with the low sulfur fuel with considerable sulfate storage. Although the sulfates accounted for 40% of the total particulate, the total particulate emission rate was sufficiently low (0.010 gms/km) that the metal oxide emission rate was 30% of the total rate. Thus it is quite possible that the relatively large contribution of metal derived exhaust particulate could have altered the particle size distribution.

IV.4.3 Particle Size Distribution, NO_x Reduction Catalyst Equipped Vehicle

With NO_x reduction catalyst equipped vehicles, the particle size distribution on the FTP's generally resembled the base case vehicles. For these tests, the cumulative % mass of particulates smaller than 2.1 microns equivalent diameter ranges from 88 to 98%, Figures IV-62 to IV-66. On the cruises, the particle size distribution resembles that of the vehicle equipped with the various oxidation catalysts. For example with a Grace reduction catalyst equipped vehicle on a 64 km/hr cruise, the cumulative % mass of particulate less than 2.1 microns was 99.6% (Figure IV-66). This was because of lean vehicle operation over a noble metal catalyst with a high sulfur fuel. The sulfuric acid emission rate in this case was 0.065 gms/km, and accounted for almost 50% of the total particulate. Under these circumstances, it is not surprising that the particle size distribution resembled that produced by oxidation catalyst equipped vehicles.

IV.4.4 Particle Size Distributions After Sulfate Storage

Figure IV-67 shows the particle size distribution obtained on the second 75 FTP of the sulfate storage test run sequence. The distribution deviates considerably from the log normal distributions exhibited on the standard oxidation catalyst screening runs Figures IV-57 to IV-61. It can be seen from Figure IV-67 that unlike the standard screening tests with the oxidation catalyst equipped vehicle, the cumulative % for particle equivalent diameters of less than 0.43 microns is about 40%. In this run, the particulate sulfate emissions exceed 100% based on fuel consumption values as a result of release of stored sulfate (Section IV.1.5). This released sulfate may have a larger particle size than sulfate produced during the run. The quantity of stored sulfate that is released must be several times that of freshly produced and emitted sulfate. Thus, the emitted sulfate as a result of storage conditioning may have two particle size distributions such that the stored sulfate has a larger mass medium equivalent diameter than freshly produced emitted sulfate.

This can be surmised by the simple expedient of assuming that the size range of released sulfate is between 0.43 and 0.65 microns, and that it would not be present in a standard screening run, a log normal distribution more nearly resembling that obtained on the standard screening test with an oxidation catalyst equipped vehicle. This plot (backing out the weight increment on the seventh impactor stage) is shown in Figure IV-64 (open circles). This approach means that about 60% of the emitted sulfate was released from storage. Although the above arithmetical manipulation is not conclusive proof of the presence of larger particle size sulfuric acid, it does substantiate the possibility of its existence. Analysis of the stages would be required to verify the altered distribution of sulfuric acid particle size as a result of release of stored sulfur.

Table IV-13

Comparison of Total Particulate Emission Rates, Andersen Impactor Versus Total Filter

Run No.	Test Type	% Fuel Sulfur	Catalyst	Total Particulate Emission Rate, gms/km as Measured by Impactor Stages + Final Filter	Total Filter
6	75 FTP	0.110	None	0.026*	0.026
9	112 km/hr	"	"	0.012*	0.009
11	75 FTP	0.091	"	0.018	0.030
14	112 km/hr	"	"	0.007*	0.008
15	75 FTP	"	"	0.018*	0.022
16	75 FTP	0.019	"	0.009	0.015
18	64 km/hr	"	"	0.0021	0.002
19	112 km/hr	"	"	0.002	0.003
20	75 FTP	"	"	0.013	0.019
29	112 km/hr	0.091	"	0.004*	0.004
36	75 FTP	0.019	Engelhard Monolith	0.012	0.031
38	65 km/hr	0.019	"	0.005	0.018
40	75 FTP	0.019	"	0.006	0.043
41	75 FTP	0.110	"	0.068	0.169
43	64 km/hr	"	"	0.004	0.262
45	75 FTP	"	"	0.007	0.150
46	75 FTP	0.091	"	0.005	0.226
48	64 km/hr	"	"	0.006	0.192
50	75 FTP	"	"	0.008	0.131
51	75 FTP	0.019	Engelhard Pellet	0.009	0.061
53	64 km/hr	"	"	0.001	0.009
55	75 FTP	"	"	0.003	0.036
56	75 FTP	0.11	"	<0.001	0.059
58	64 km/hr	"	"	0.003	0.246
60	75 FTP	"	"	0.005	0.083
61	75 FTP	0.091	"	0.003	0.062
63	64 km/hr	"	"	0.201	0.002
65	75 FTP	"	"	0.002	0.201
66	75 FTP	0.019	UOP(1)	0.002	0.029
68	64 km/hr	"	"	0.011	0.037
70	75 FTP	"	"	0.005	0.035
71	75 FTP	0.110	"	0.012	0.104
73	64 km/hr	"	"	0.342	0.490
75	75 FTP	"	"	0.013	0.090
76	75 FTP	0.091	"	0.005	0.134
78	64 km/hr	"	"	0.149	0.462
80	75 FTP	"	"	0.009	0.042

Table IV-13 (Cont'd.)

Run No.	Test Type	% Fuel Sulfur	Catalyst	Total Particulate Emission Rate, gms/km as Measured by	
				Impactor Stages + Final Filter	Total Filter
81	75 FTP	0.019	Matthey Bishop	0.012	0.028
83	64 km/hr	"	"	0.009	0.014
85	75 FTP	"	"	0.021	0.009
86	75 FTP	0.110	"	0.047	0.086
88	64 km/hr	"	"	0.092*	0.118
90	75 FTP	"	"	0.011	0.050
91	75 FTP	0.091	"	0.030	0.069
93	64 km/hr	"	"	0.058	0.087
95	75 FTP	"	"	0.011	0.040
96	75 FTP	0.019	Grace Reduction	0.006*	0.007
98	64 km/hr	"	"	0.003	0.005
100	75 FTP	"	"	0.006	0.017
101	75 FTP	0.110	"	0.015*	0.016
103	64 km/hr	"	"	0.125*	0.133
105	75 FTP	"	"	0.007	0.019
106	75 FTP	0.091	"	0.008	0.020
108	64 km/hr	"	"	0.118	0.069
110	75 FTP	"	"	0.011	0.041
111	75 FTP	0.019	Gould Reduction	0.017	0.041
113	64 km/hr	"	"	0.005*	0.005
115	75 FTP	"	"	0.008	0.013
116	75 FTP	0.110	"	0.009	0.025
118	64 km/hr	"		0.072	0.116
120	75 FTP	"	"	0.016*	0.016
121	75 FTP	0.091	"	0.008	0.031
123	64 km/hr	"	"	0.054	0.089
125	75 FTP	"	"	0.020*	0.019
126	75 FTP	0.019	Grace Pellet	0.006	0.044
128	64 km/hr	"	"	0.008	0.016
130	75 FTP	"	"	0.009	0.026
131	75 FTP	0.110	"	0.016	0.027
133	64 km/hr	"	"	0.172*	0.177
135	75 FTP	"	"	0.038	0.065
136	75 FTP	0.091	"	0.018	0.066
138	64 km/hr	"	"	0.133*	0.140
140	75 FTP	"	"	0.011	0.051
141	75 FTP	0.019	UOP(2)	0.013	0.023
143	74 km/hr	"	"	0.018	0.025
145	75 FTP	"	"	0.007	0.014
146	75 FTP	0.110	"	0.041	0.070
148	64 km/hr	"	"	0.014	0.363
150	75 FTP	"	"	0.011	0.151
151	75 FTP	0.091	"	0.012	0.173
153	64 km/hr	"	"	0.012	0.119
155	75 FTP	"	"	0.026	0.134

Table IV-13 (Cont'd.)

				Total Particulate Emission Rates, gms/km as Measured by	
Run No.	Test Type	% Fuel Sulfur	Catalyst	Impactor Stages + Final Filter	Total Filter
156	75 FTP	0.019	Air Products	0.011	0.034
158	64 km/hr	"	"	0.005	0.020
160	75 FTP	"	"	0.009*	0.010
161	75 FTP	0.110	"	0.007	0.051
163	64 km/hr	"	"	0.013	0.149
165	74 FTP	"	"	<0.001	0.106
166	75 FTP	0.091	"	0.036*	0.043
168	64 km/hr	"	"	0.060	0.163
170	75 FTP	"	"	0.023	0.123
171	75 FTP	0.019	Engelhard Pellet**	0.020	0.105
173	64 km/hr	"	"	0.054	0.258
175	75 FTP	"	"	0.132*	0.152

** Runs 171-175 are sulfate storage runs.

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APPENDIX A

ANALYTICAL METHODS

A.1 Analytical Determination of Sulfate

In earlier in-house work on sulfate emissions, sulfate was determined gravimetrically by a modification of the standard gravimetric method for sulfate, ASTM Procedure D1099(1). This has been superceded by a titrimetric procedure for sulfate using a color indicator. Sulfonazo III [4,5-dihydroxy-3,6-bis(o-sulphophenylazo)-2,7 naphthalene-disulfonic acid]. The procedure has been adapted from that of Budesinsky and Krumlova(2).

The soluble sulfate collected by the filter in the exhaust particulate sampler is leached from the filter with dilute nitric acid. The leach solution is heated to boiling to drive off excess nitric acid, filtered to remove insoluble material, passed through an ion-exchange column to remove interfering cations, and then buffered with methenamine to a pH of 3-4. The resulting solution is titrated with barium perchlorate using Sulfonazo (III) as the indicator.

A.1.1 Reagents

The reagents used are as follows:

1. Barium perchlorate standard solution 0.01N
2. Barium perchlorate standard solution 0.001N
3. Hexamethylenetetramine (5% aqueous)
4. Sulfonazo III indicator (0.1 g/100 ml H_2O)
5. Ethyl Alcohol, absolute
6. Acetone
7. Nitric acid (2% aqueous)
8. Dowex 50 W-X8 cation exchange resin (50-100 mesh)

A.1.2 Titration Apparatus

The following apparatus was used in the titrations:

1. Ion exchange column, 1 cm x 25 cm.
2. Burettes (at least 0.05 ml div)
3. Low range pH paper - J. T. Baker Dual-Tint pH 1.0-4.3.

A.1.3 Standardization of $Ba(ClO_4)_2$ Solution

The barium perchlorate solution is standardized by titration against previously standardized 0.01N sulfuric acid as follows:

(1) 5 mls of 0.01N sulfuric acid is pipetted into a 125-ml Erlenmeyer flask.

(2) 45 mls of deionized water and 2.5 mls 2% nitric acid are added.

(3) Adjust the pH as described in the Procedure and titrate with barium perchlorate solution.

(4) Calculate normality.

$$N \quad Ba(ClO_4)_2 = \frac{\text{mls } H_2SO_4 \times N \quad H_2SO_4}{\text{mls } Ba(ClO_4)_2}$$

A.1.4 Detailed Titration Procedure

(1) Cut and place 1/4 section of filter in 100-ml beaker. (1/2 filter can be used for lower levels of SO_4).

(2) Add 3.0 mls of 2% nitric acid, wetting the filter section completely.

(3) Add 20 mls of deionized water.

(4) Place small glass stirring rod in beaker and cover with watch glass.

(5) Digest samples on hot plate and allow to boil for 5 minutes.

(6) Cool beakers and filter liquid through glass wool into the ion-exchange column containing ~7.5 g of Dowex 50 W-X8 cation exchange resin, collecting sample in 125 ml Erlenmeyer flasks.

(7) Wash beaker with 3 x 5 ml portions of deionized water. Add washings to column. After each washing, squeeze liquid from the filter by pressing it against the wall of the beaker with the stirring rod.

(8) Place the flask on a hot plate and evaporate to approximately 5 mls.

(9) Adjust the pH of the remaining solution to pH 4 using 5% hexamethylenetetramine.

(10) Add 10 mls ethyl alcohol and 25 mls acetone to the flask.

(11) Add 3 drops Sulfonazo III indicator.

(12) Titrate with 0.01N barium perchlorate solution. (If sulfate content is low, use 0.001N barium perchlorate.) If the sample

requires more than 10 mls of barium perchlorate to reach the end point the results are unreliable and should be discarded. Another portion of filter should be treated as in steps 1-7. Solution should be collected in 100 ml volumetric flask. An appropriate size aliquot is taken and the test is continued with step 8.

A.1.4.1 Effect of Nitric Acid on Measurement of Sulfate

Because nitric acid is used as the leaching agent, several experiments to ascertain the effect if any of nitric acid on the determination of sulfate were carried out. The test matrix, shown in the following table, shows that there is no effect of nitric acid on the titration.

Table A-1

Comparative Titrations of Sulfate of Samples With and Without Nitric Acid

Sample	Contains HNO_3	ml 0.012 N $Ba(ClO_4)_2$ to Titrate Theory	Actual	Δml
$Na_2SO_4 \cdot H_2SO_4$	Yes	5.0	4.9	-0.1
$Na_2SO_4 \cdot H_2SO_4$	No	5.0	4.7	-0.3
H_2SO_4	Yes	5.0	4.7	-0.2
H_2SO_4	No	5.0	4.8	-0.2

A.1.4.2 Precautions About Titration Procedure

The above procedure was arrived at after experimental work identifying sources of error and the means to minimize or eliminate these errors was worked out. Reliable results can be obtained if the following precautionary measures are taken:

(1) Keep HNO_3 at minimum
(2) Keep water in sample at minimum
(3) pH is very critical (~4.0)
(4) Use blank for color comparison of end point
(5) Change Dowex frequently (approx. 3 samples)
(6) If sample is basic - adjust with Nitric Acid

For example, it was shown that not only is the ion-exchange step necessary to eliminate interference, but that it is necessary to insure that the capacity of the ion-exchange bed is not close to exhaustion. It was also shown that it is necessary to use a new batch of ion-exchange resin rather than a regenerated batch. Positive deviations were obtained when titrating the effluent from a regenerated ion-exchange bed. The results of the tests described above are shown in Table A-2.

Table A-2

Experiments Demonstrating Influence of Ion Exchanger on Sulfonazo III End Points

Mls. H_2SO_4	Mls. Titration Theory	Mls. Titration Actual	Δml	
Blank	0.0	0.1	+0.1	
0.5	0.5	0.5	0	
0.75	0.75	0.65	-0.1	Same column for all samples 0.012 N $Ba(ClO_4)_2$
1.00	1.00	1.0	0	
1.50	1.50	1.25	-0.25	
2.00	2.00	1.45	-0.55	
2.00	2.00	2.2	+0.20	
1.50	1.50	1.75	+0.25	New Dowex each sample 0.012 N $Ba(ClO_4)_2$
1.00	1.00	1.1	+0.10	
Blank	0	0.15	+0.15	
0.2	2.0	2.10	+0.10	
0.5	5.0	4.95	-0.05	0.0012 N $Ba(ClO_4)_2$
0.1	1.0	1.45	+0.45	
0.8	0.8	0.80	0	
1.0	1.0	1.00	0	New Dowex 0.012 N Ba $(ClO_4)_2$
2.0	2.0	1.90	-0.10	
Blank	0	0.25	+0.25	
0.1	1.0	2.10	+1.10	
0.1	1.0	2.00	+1.00	Regenerate Dowex with 1:5 HCl
0.2	2.0	2.90	+0.90	
0.2	2.0	3.00	+1.00	0.0012 N $Ba(ClO_4)_2$
2.0	2.0	1.30	-0.7	
2.0	2.0	1.40	-0.6	0.012 N Ba $(ClO_4)_2$

As shown above, the Dowex ion exchanger has to be changed frequently, and that large errors result if one attempts to work with a presumably regenerated ion exchanger. Satisfactory results can be obtained if the Dowex resin is changed after every two to three determinations.

A.1.5 Sulfate Determinations on Glass Fiber Filters Spiked with Known Quantities of H_2SO_4

A series of filters were spiked with known quantities of H_2SO_4 using 1.000 N H_2SO_4 and a 5 µl syringe and with 0.0112 N H_2SO_4 solutions. The filters were leached with water, the leach solution worked up for

for analysis as discussed in Section A.1.4. Figure A-1 shows a plot of added sulfate versus sulfate recovered by titration. It can readily be seen that analysis of sulfate on the filters is as reliable as analysis of solutions containing known quantities of sulfate. The next step was to determine if this method is workable with filters containing actual auto exhaust since the presence of organic exhaust particulate matter on these filters could possibly introduce substances which interfere with the color change of the titrimetric procedure. To determine if such interferences existed, the procedure was then checked against the gravimetric determination of sulfate on parallel filters from actual vehicle test runs since the presence of organic materials would have no effect on the latter determination.

A.1.6 Comparison of Titrimetric and Gravimetric Procedures on Filters from Vehicle Tests

Comparisons were then made between the titrimetric and gravimetric analytical procedures on particulate filters from actual vehicle runs. The titrimetric analysis was carried out on quarter sections of the filters, the gravimetric on an entire parallel filter. The particulate filters were generated from vehicles equipped with pelletized and monolithic catalysts, operating on fuels of sulfur levels ranging from 0.004 to 0.14 wt %. Both cyclic and steady state test modes were used. The results are shown in Table A-3.

Table A-3

Comparison of Titrimetric and Gravimetric $SO_4^=$ Analyses on Parallel Filters

(Actual Vehicle Runs, Sample Data)

Run Type	Fuel Sulfur, %	Catalyst Type	$SO_4^=$ Emissions, g/mi. Titrimetric	$SO_4^=$ Emissions, g/mi. Gravimetric
40 mph, 1/2 hr.	0.14	Pelletized	0.036	0.040
1975 FTP	0.065		0.012	0.011
1975 FTP	0.056		0.0099	0.0081
40 mph, 1 hr.	0.004	↓	0.004	0.004
1975 FTP	0.14	Monolith	0.306	0.287
			0.296	0.288
	↓		0.176	0.173
	0.004		0.053	0.061
↓			0.023	0.020
	↓		0.029	0.020
60 mph, 20 min.	0.14		0.259	0.239
			0.294	0.253
	↓		0.265	0.247
	0.004		0.009	0.007
↓	↓	↓	0.011	0.008
			0.011	0.008

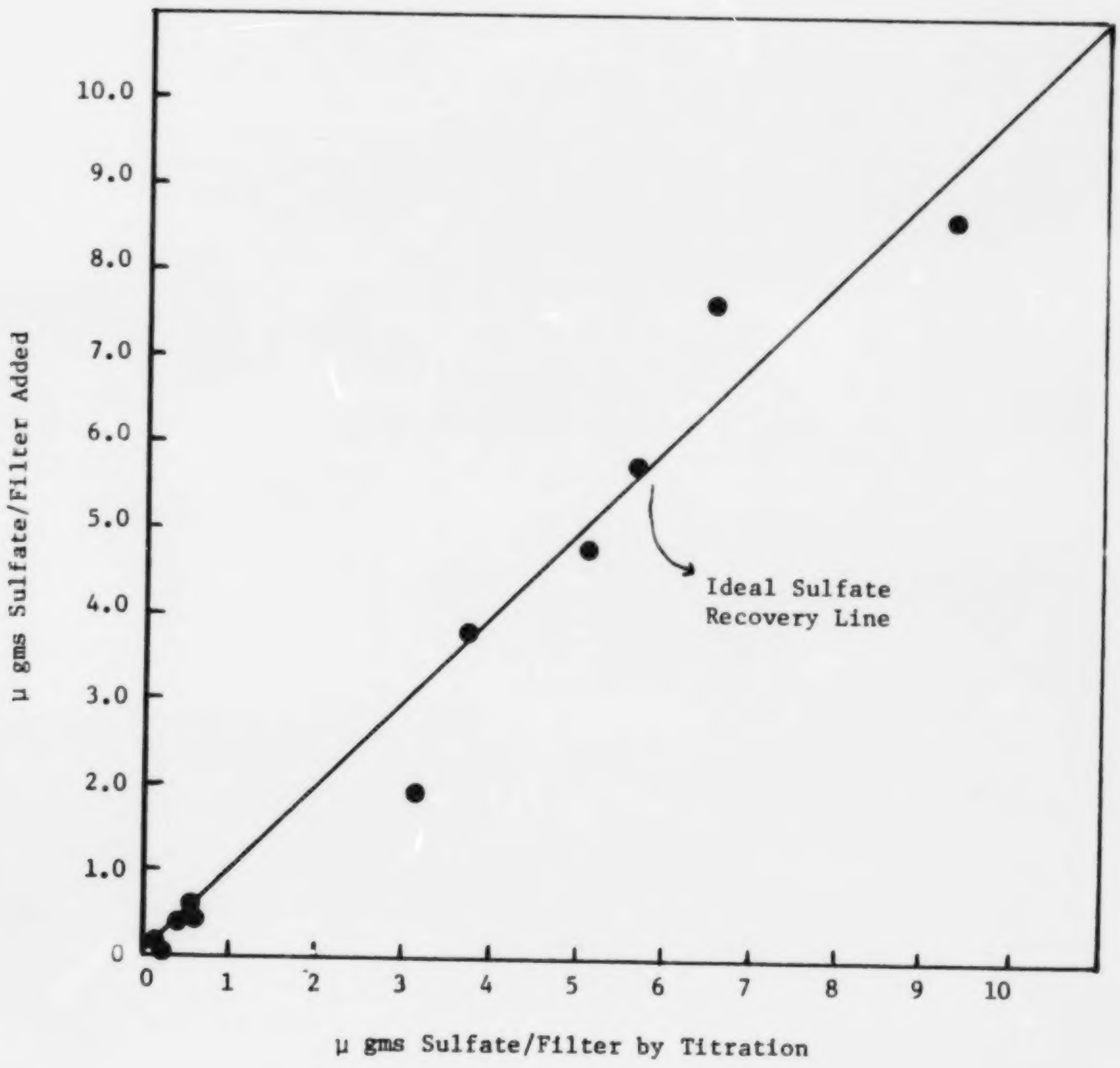
Regression analysis on 26 comparison sets showed:

$$\text{Titrimetric } SO_4^= = 1.029 \text{ Gravimetric } SO_4^= + 0.00085$$

Standard Deviation = 0.01

Figure A-1

Recovery of Sulfate From Spiked Glass Fiber Filter Samples



A.2 Sulfur Dioxide Determination

Sulfur dioxide in diluted automotive exhaust was measured using a Thermo Electron Corporation (TECO Model 40) Sulfur Dioxide Analyzer(3). This device operates on a pulsed-fluorescence UV absorption principle as follows. A gas sample is submitted to a source of pulsed ultraviolet light through a monochromatic filter. Sulfur dioxide molecules energized to an excited state by the high intensity light source, return to the ground state by emitting a monochromatic light, which passes through a narrow-band filter, and impinges upon the light sensitive surface of a photomultiplier tube. The intensity of this radiation is directly proportional to the SO_2 concentration.

This measurement method was chosen because of the following reasons:

(1) It is more convenient than wet chemical, conductimetric, or coulometric methods.

(2) Both continuous and integrated measurements of SO_2 in diluted exhaust can be made.

(3) Measurement of SO_2 emission rates could be incorporated as part of the gaseous emission measurements routinely obtained using diluted exhaust collected by the CVS system.

The operating principle of the TECO analyzer is depicted schematically in Figure A-2.

To eliminate the possibility of water adsorbing and condensing in the sample chamber on the walls and optical filters, the water in the sample stream was removed upstream to the TECO analyzer. Initially, Drierite was used to remove the water but it was found that at the 5 to 10 ppm level of SO_2, the Drierite absorbed all the SO_2.

The water removal problem was solved by using the Permatube Drying System(4) shown in Figure A-3. This system dries the sample stream by passing it through a bundle of tubes which are permeable to water but essentially impermeable to SO_2. Water is purged by countercurrent flow of dry air or nitrogen. The effectiveness of the permeable system in reducing the water level of a humid sample stream below 10 ppm H_2O while retaining the SO_2 in the sample has been established by our Analytical Division. The Model PD-500-72 Perma Pure Dryer according to the manufacturer (4) has the capability of taking a feed having a 120°F dew point and extracting sufficient water at a 4 to 6 SCFH feed rate to reduce the dew point of the effluent to -25°F.

Figure A-2 Principle of Operation
TECO SO_2 Instrument

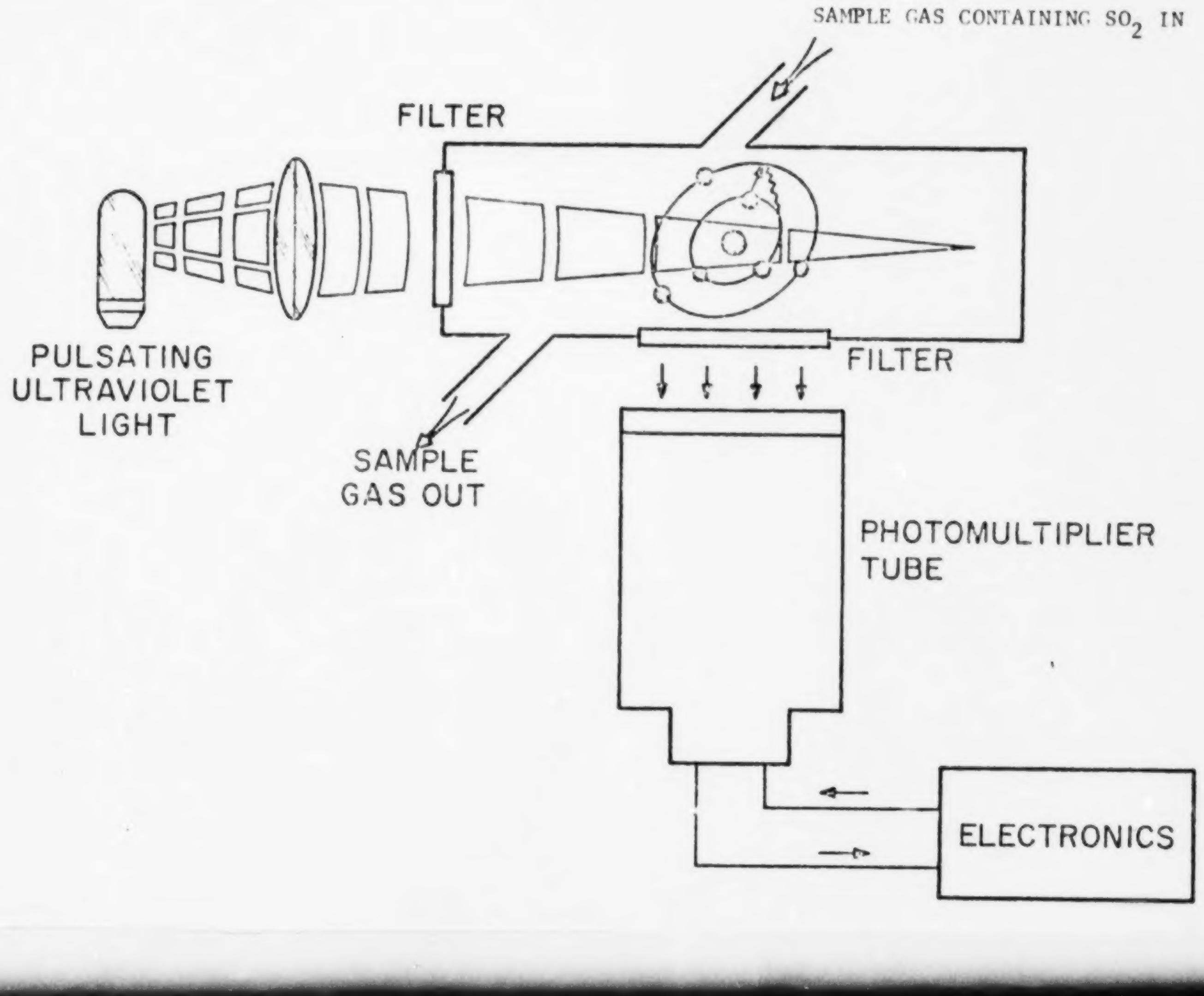
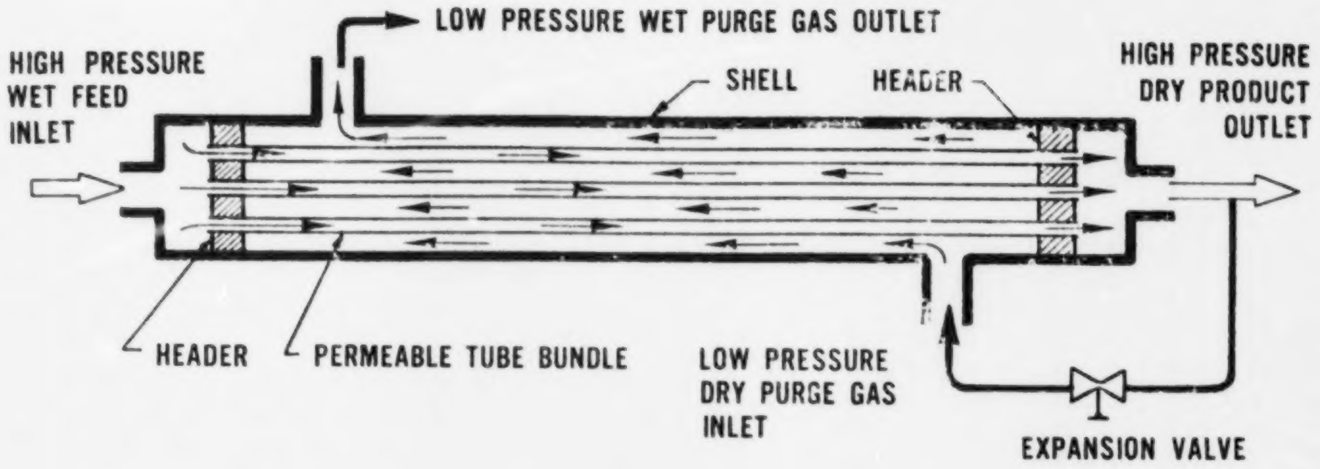


Figure A-3

Permatube Drying System


LOW PRESSURE WET PURGE GAS OUTLET
HIGH PRESSURE WET FEED INLET
SHELL
HEADER
HIGH PRESSURE DRY PRODUCT OUTLET
HEADER
PERMEABLE TUBE BUNDLE
LOW PRESSURE DRY PURGE GAS INLET
EXPANSION VALVE

Our own tests with dry [SO_2 in N_2 and in air] have shown that no differences in TECO readings were obtained when the sample is introduced directly into the analyzer, or when it passes through the dryer prior to entry into the analyzer.

A millipore filter is used upstream to the dryer to prevent any particulate matter from entering and eventually clogging the dryer, and for that matter, from possibly entering and contaminating the analyzer.

It has been found that CO_2, CO, and O_2 are strong quenching agents, while N_2 exhibits a negligible quenching effect. The instrument response is therefore sensitive to background gas composition. Absolute values of SO_2 concentrations necessitate calibration of the instrument in a background representative of the sample to be analyzed.

For example, prior to a laboratory study on SO_2 conversion as a function of oxygen concentration, it was necessary to assess the effect of oxygen quenching(5). Various amples were made by preparing bell jar mixtures containing 30 ppm SO_2, 12% CO_2, varied amounts of oxygen, and nitrogen as the balance gas. Measurements of the SO_2 concentration of these mixtures indicate an approximate 1 ppm reduction in instrument SO_2 response for each 2% increment in oxygen concentration, as shown below.

Table A-4

SO_2 Measurements at Indicated Oxygen Concentrations(a)

Oxygen Concentration (%)	TECO SO_2 Response (ppm)
0	29.7
1	28.8
2	28.4
4	26.8
6	26.2

(a) Basic Mixture, 30 ppm SO_2, 12% CO_2, balance N_2.

The quenching effects of CO and CO_2 was also measured using mixtures of 30 ppm SO_2 in pure CO and CO_2. In CO_2, the response to 30 ppm of SO_2 was 1.7 ppm, that in CO only 8.5. Measurements were then carried out on bell jar mixtures of 30 ppm of SO_2 in background air containing different concentrations of CO, O_2, C_3H_8, and CO_2. The results given below show that instrument response is sensitive to overall concentration of quenching species. Therefore data obtained where the total background concentration

Table A-5

Composite Effects of CO_2, O_2 and CO on TECO SO_2 Response

Mixture Composition	Total Quencher Species Concentration (%) $[CO_2] + [O_2] + [CO]$	Instrument Response (ppm)
30 ppm SO_2 1.42% O_2 0.09% CO 0.051% H_2 445 ppm C_3H_8 12.5% CO_2	14.0	28
30 ppm SO_2 4.78% O_2 14.3% CO_2 4.33% CO 348 ppm C_3H_8	23.4	23

of quenching species changes significantly from the calibration gas quencher level should be corrected for the inherent changes in instrument response.

For vehicle work, quenching effects are minor. Quenching by exhaust CO_2 and CO is negligible for a CVS air diluted sample due to dilution. Although the oxygen concentration increases with dilution, it presents a reasonably constant quench background and can be taken into account by calibration of dilute SO_2 in air mixtures. Properly used, the precision of this instrument is about 0.5 ppm SO_2.

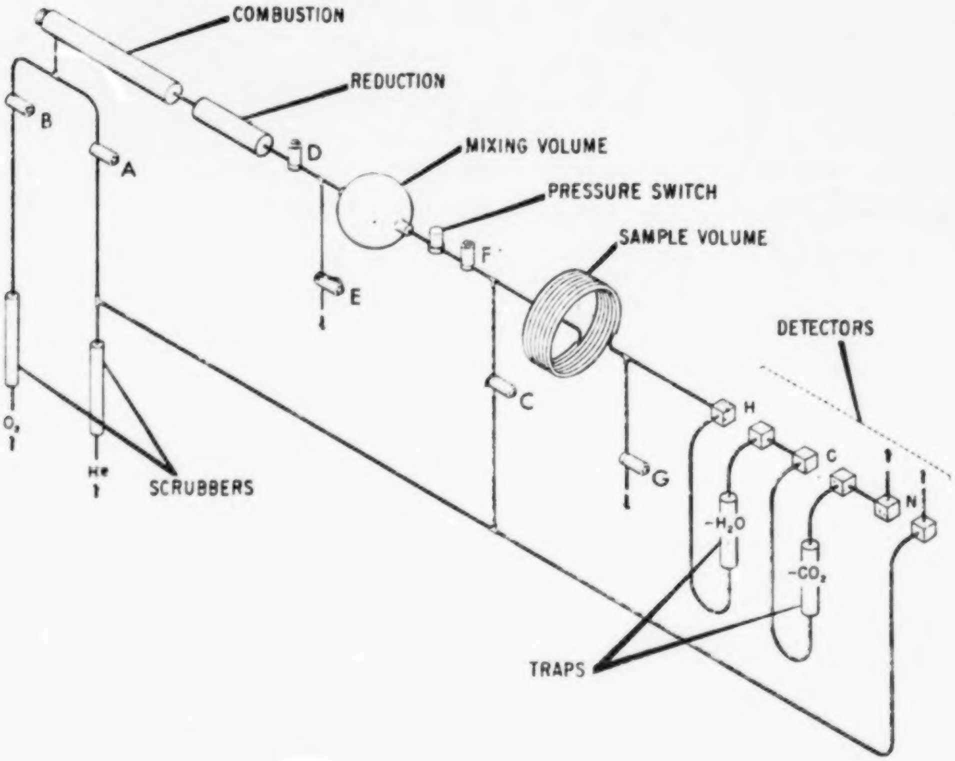
A.3 Carbon, Hydrogen, and Nitrogen Determinations

Carbon, hydrogen, and nitrogen was measured by gas chromatography. A portion of the glass fiber filters was inserted into the combustion tube of a Perkin-Elmer Model 240 C/H/N microanalyzer. A schematic of the detection system of this device is shown in Figure A-4.

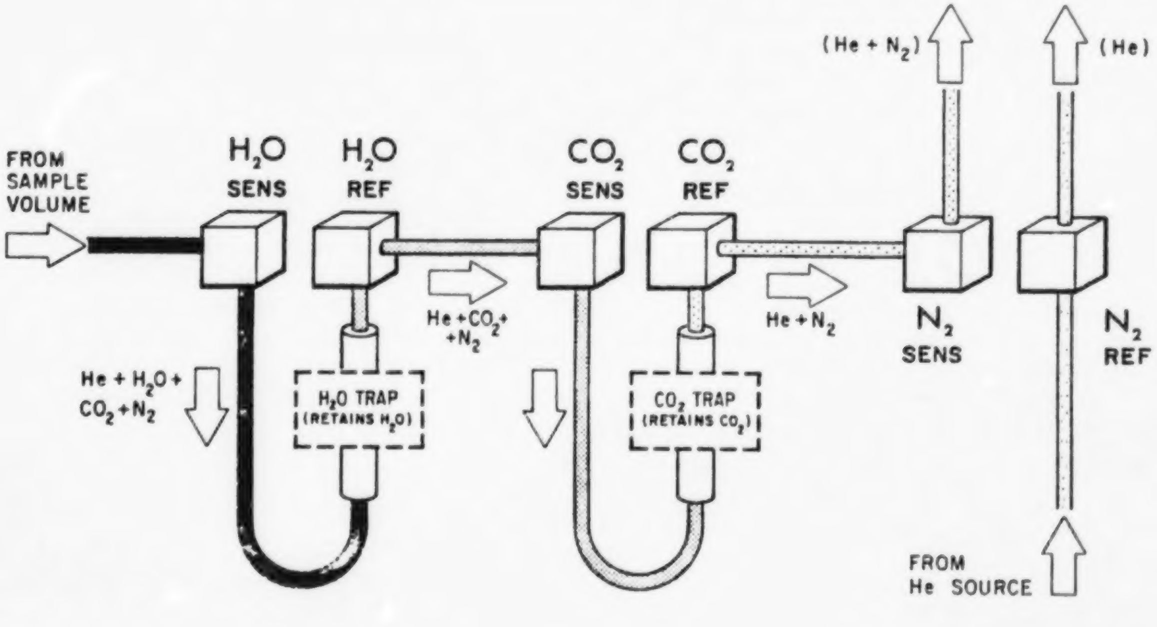
Combustion of the samples occurs in pure oxygen. The products of combustion are carried into a reduction zone which includes: silver tungstate on magnesium oxide, silver oxide and silver tungstate on chromosorb P, silver vanadate, and silver gauze. The purpose of this reduction zone is to insure that combustion is complete and that interfering combustion products (such as SO_2) are removed. The gas leaving the reduction zone contains only CO_2, H_2O, N_2, and He.

FIGURE A-4

PERKIN-ELMER MODEL 240 C/H/N MICROANALYZER



Simplified Diagram of Combustion Train and Analytical System



These gases are flushed into a closed, spherical glass mixing volume and additional helium added until the pressure reaches 1500 mm Hg. The contents of the mixing volume remain there for 90 sec. in order to reach a homogenous composition. When mixing is complete, the contents of the mixing volume expand through the sample volume detectors and out to the atmosphere.

Three pairs of thermal conductivity cells, in series, are used for detection - one pair each for water, carbon dioxide, and nitrogen. The platinum filaments of each cell pair are connected differentially in a bridge circuit so that any difference in the contents of the two cells will result in an electrical signal.

A magnesium perchlorate trap between the first pair of cells absorbs any water from the gas mixture before it enters the second cell so that the signal obtained from the corresponding bridge circuit is proportional to the amount of water removed. Likewise, an absorbing trap between the second pair of cells results in a signal proportional to the carbon dioxide removed. The last pair of cells detects nitrogen by comparing the thermal conductivity of the remaining sample gas to that of pure helium.

The normal sample size used with the C/H/N analyzer is 2 mg and accuracy of 0.3% is obtainable. This places the minimum detectible amount of C, H, and N at ~6 μg. Only a portion of the filter can be used because of the small combustion tube in this unit. If 25% of the filter were used the minimum detectible emission rate would be ~ 6×10^{-5} g/mi of C, H, or N on the 1975 FTP or ~ 2.5×10^{-5} g/km of C, H, or N on the 2 hr., 70 mph cruise mode.

It should be noted that the hydrogen measurement obtained by this technique includes hydrogen present in the particulate in water of hydration. The amount of water of hydration can be determined separately using the Karl Fisher titration technique. It would not be justified to determine water routinely by Karl Fisher titration and also determine total hydrogen by the semi-micro combustion technique. This is because data we have collected in previous work(6) show that most of the hydrogen in particulate is present in water of hydration. To then determine organic hydrogen as the small difference between two large numbers would result in a highly inaccurate value.

A.4 Characterization of Specific Compounds in Automotive Exhaust Particulate

A.4.1 Bound Water

Bound water is determined by the Karl Fisher titration technique. This technique makes use of the fact that water enters many reactions such as the redox reaction:

$$I_2 + SO_2 + 2\ H_2O \longrightarrow 2\ HI + H_2SO_4$$

If this reaction is carried out in a non-aqueous medium it can be used to quantitatively determine water. The reaction actually used is

$$H_2O + I_2 + SO_2 + CH_3OH + 2\ Py \longrightarrow CH_3HSO_4 + 2\ Py.HI$$

whose Py = Pyridine. The Karl Fisher reagent is prepared from anhydrous methanol, anhydrous pyridine, iodine and sulfur dioxide. A small sample of the filter is soaked in anhydrous methanol then titrated with the Karl Fisher reagent to an end point determined by the appearance of excess iodine.

The procedure used at Exxon is based on ASTM E203(7). The titration is carried out to an electrometric end point using a commercial titration assembly in which the titration is automatically stopped at the end point(8). The least detectible amount of water is about 10 µgms, although accuracy will suffer if 100 µgms of H_2O is not obtained. If one-fourth of a filter is used for analysis, 100 µgms of H_2O corresponds to a water emission rate of 6.8×10^{-4} gms/km for a 1975 FTP.

A.4.2 Organic Nitrogen Compounds

A.4.2.1 Nitrogenous Particulate

Chemical spot tests were carried out on particulate samples generated from the 1975 FTP and 64 km/hr (40 mph) test runs for nitrogenous particulate and non-sulfate sulfur containing particulate matter. The samples analyzed were from runs with the unequipped vehicle, and with the vehicle equipped with the catalysts that were tested in the contract program. The spot tests used were adapted from Feigl(8).

The sensitivity of many of these tests is such that low levels of nitrogenous and non-sulfate particulate matter should be readily detectible. Negative tests for a given compound or compound type establishes the maximum emission rate possible based on the sensitivity of the spot test, the mileage accumulated on the particular test run, and the size of the filter portion used for analysis. Because of the many analyses that were conducted on the particulate filters, only a small portion (0.385 cm^2) was selected for a given spot test. Thus, the maximum emission rate (ERM), in gms/km for a given organic compound based on a negative test result is:

$$\text{ERM} = \frac{(\text{DL})}{\Delta(\text{km}) \times F_1 \times F_2} \quad \text{where:}$$

DL = chemical detection limit in grams
Δ(km) = distance accumulated on the particulate in kilometers
F_1 = volume fraction of diluted auto exhaust sampled
F_2 = fraction of active filter area used for the chemical spot test

Obviously by varying F_1 and F_2, the maximum emission rate can vary over a wide range. The volume fraction of diluted exhaust sampled F_1, is fixed by our sampling tunnel and probe dimensions consistent with isokinetic sampling. Larger filter areas could be used for analysis if the need arose. Presently 0.42% of the active filter area (0.39 cm^2) is used for each chemical spot test. Maximum emission rates based on a filter area of 0.39 cm^2 generally range from 10^{-5} to 10^{-3} gms/km for the 1975 Federal Test Procedure, and 10^{-6} to 10^{-3} gms/km for the 64 km/hr one-hour cruise. As mentioned above, the filter area selected for testing was based solely on practical considerations. The range of maximum emission rates based on this area are generally considered insignificant, unless some unusually toxic or reactive component was involved. Figures A-5 and A-6 depict the analytical test scheme for what are considered to be chemically logical, possible exhaust nitrogenous and sulfur (excluding sulfate) containing exhaust components. The nitrogen compounds tested for were:

nitroparaffins, nitroaromatics
organic nitrates, nitrites, nitroamines, and nitrosamines
aliphatic and aromatic nitriles

A.4.2.2 Organic Nitrogen Compounds

The detection method used is described in Feigl, pages 90-92. This test is valid for any type of nitrogenous organic compound. The detection limit is 0.02 to 0.03 μgm of nitrogen. Using a circular cut of filter 0.39 cm^2, the detection limit corresponds to emission rates of 1×10^{-5} gms/km for the 1975 FTP and 2.5×10^{-6} gms/km for the 64 km/hr, one-hour cruise. If necessary, still lower emission rates could be determined by simply taking larger filter areas for analysis.

A.4.2.3 Compounds Containing Nitrogen and Oxygen Bonded Together

The method used is described in Feigl, pages 93-94. The detection limit is about 0.1 to 0.2 μgm for a wide variety of compounds with functional groups containing both nitrogen and oxygen, in which the weight fraction of the functional group is small.

Figure A-5

Analytical Scheme for Nitrogen Compounds in Auto Exhaust Particulate

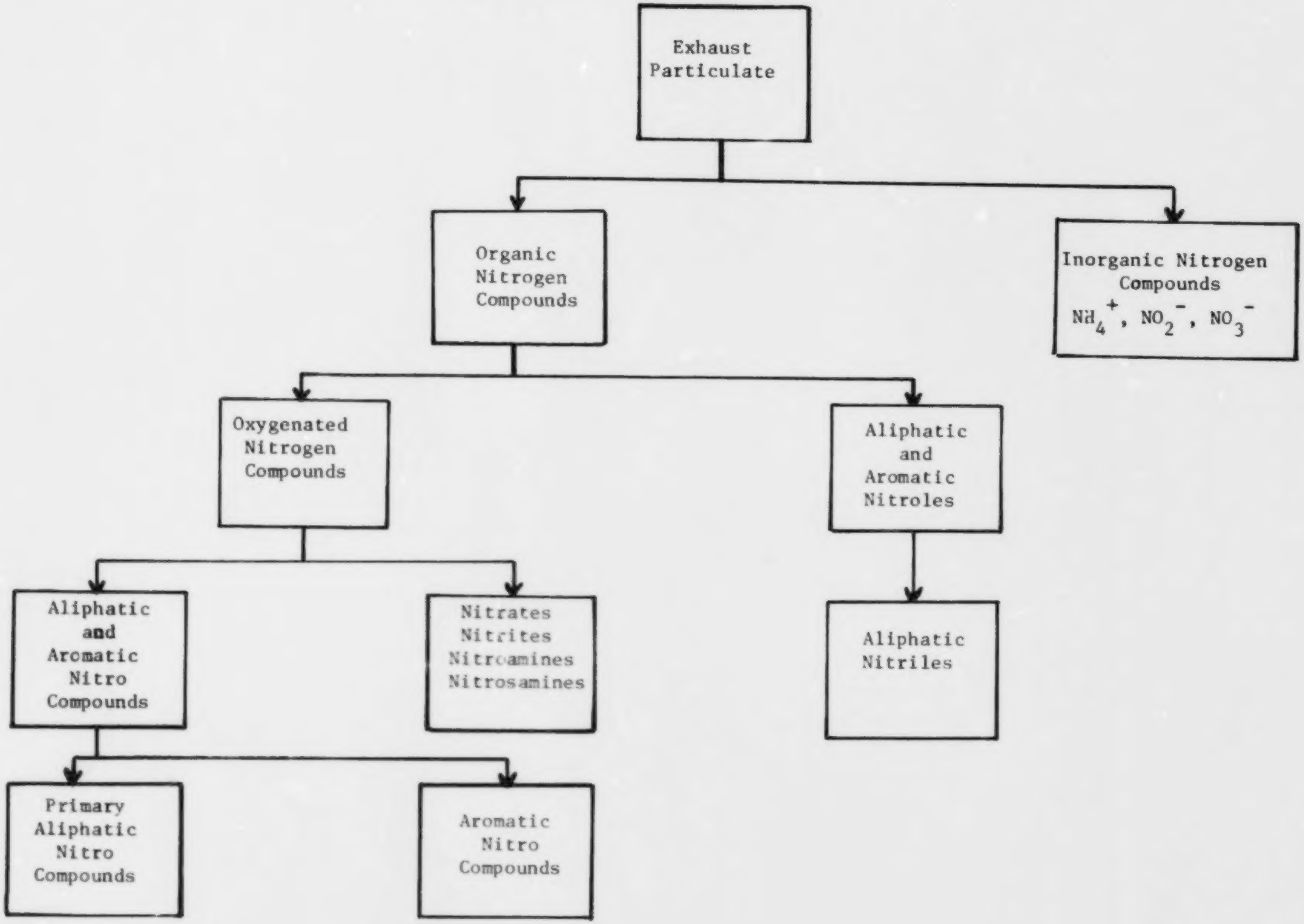
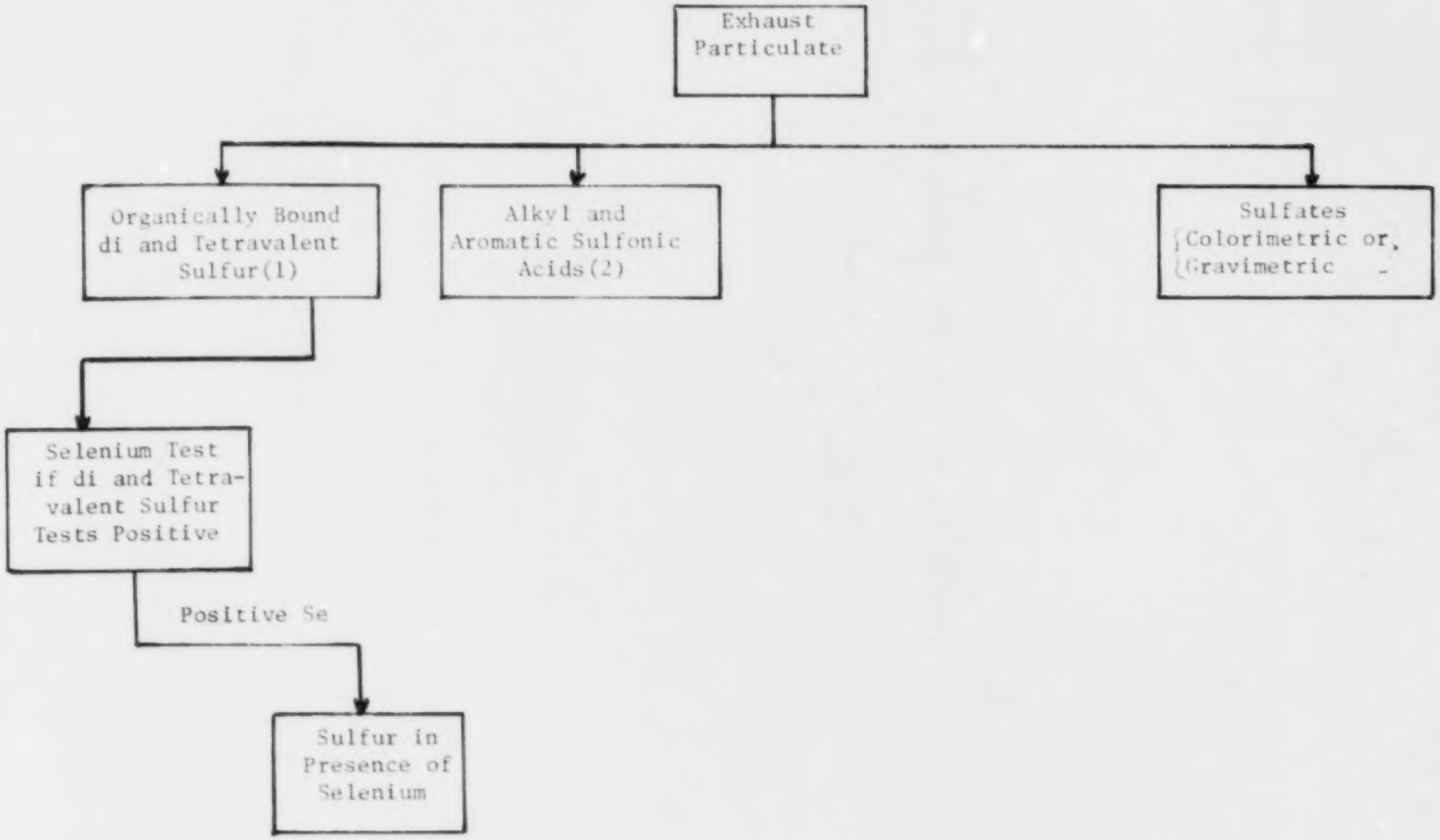

Exhaust Particulate
Organic Nitrogen Compounds
Inorganic Nitrogen Compounds NH_4^+, NO_2^-, NO_3^-
Oxygenated Nitrogen Compounds
Aliphatic and Aromatic Nitroles
Aliphatic and Aromatic Nitro Compounds
Nitrates Nitrites Nitroamines Nitrosamines
Aliphatic Nitriles
Primary Aliphatic Nitro Compounds
Aromatic Nitro Compounds

Figure A-6

Analytical Scheme for Sulfur Compounds in Exhaust Particulate


Exhaust Particulate
Organically Bound di and Tetravalent Sulfur(1)
Alkyl and Aromatic Sulfonic Acids(2)
Sulfates (Colorimetric or, Gravimetric -
Selenium Test if di and Tetravalent Sulfur Tests Positive
Positive Se
Sulfur in Presence of Selenium

Thus, negative tests for these compounds correspond to an upper emission rate of about 2 x 10^{-4} gms/km for the 1975 FTP and 5 x 10^{-5} gms/km for the 64 km/hr, one-hour cruise. The following compounds can be detected:

- C - Nitro compounds
- N - Nitro compounds
- C - Nitroso compounds
- N - Nitroso compounds
- Hydroxamic acids
- Oximes
- Azoxy and hydroxyl amine compounds
- Nitrates
- Nitrites
- Nitramines
- Amine Oxides

A.4.2.4 Aliphatic and Aromatic Nitro Compounds

The detection method used is described in Feigl, pages 295-297, included tests for primary aliphatic nitrocompounds. The detection limits for general nitrocompounds were about 0.5 to 1μgm corresponding to an emission rate ranging from 2 to 4 x 10^{-4} gms/km for the 1975 FTP and 5 x 10^{-5} to 1 x 10^{-4} gms/km for the 64 km/hour, one-hour cruise.

For primary aliphatic nitro compounds such as nitromethane, nitroethane, and nitropropane, the emission rates corresponding to the detection limits are 2 x 10^{-4} gms/km for the 1975 FTP and 5 x 10^{-5} gms/km for the 64 km/hours, one-hour cruise.

The detection method for aromatic nitro compounds is described in pages 297-298 of Feigl and is sensitive to about 1.5 μgms of nitrobenzene corresponding to an emission rate 6 x 10^{-4} gms/km for the 1975 FTP and 1.5 x 10^{-4} gms/km for the 64 km/hr, one-hour cruise.

A.4.2.5 Nitrates, Nitrites, Nitroamines, Nitrosamines

The methods used are described in pages 300-302 of Feigl. Depending upon which reagent is used, the detection limits range from 0.5 to 0.07 μgms of nitrate, corresponding to emission rates ranging from 3 x 10^{-5} to 2 x 10^{-4} gms/km for the 1975 FTP and 8 x 10^{-6} to 5 x 10^{-5} gms/km for the 64 km/hr, one-hour cruise.

A.4.2.6 Nitriles

The detection method is described in pages 264-265 of Feigl. The detection limit ranges from 2 to 20 μgms corresponding to emission rates ranging from (8 x 10^{-4} to 8 x 10^{-3} gms/km) for the 1975 FTP and (2 x 10^{-4} to 2 x 10^{-3} gms/km) for the 64 km/hr, one-hour cruise.

The detection method used for aliphatic nitriles is described in Feigl, pages 265-266 is sensitive in 2.5 to 150 μgm range. These detection limits correspond to an emission range rate of 10^{-3} to 6×10^{-2} gms/km for the 1975 FTP, and 2.5×10^{-4} to 1.5×10^{-2} gms/km for the 64 km/hr, one-hour cruise. Most of the aliphatic nitriles can be detected 2 to 20 μgm range.

A.4.3 Organic Sulfur Compounds

A.4.3.1 Organically Bound Di-and Tetravalent Sulfur

The methods used are described in pages 82 and 85 in Feigl. Compounds which contain di- and tetravalent sulfur are:

thiocarbonyls
thiols
sulfides (open and cyclic thioethers)
disulfides
thiocyanates
isothiocyanates
sulfoxides
sulfinic acids

The general test (pages 82-83) for the above compounds can detect about 2 μgm quantities corresponding to a 1975 FTP emission rate of 8×10^{-4} gms/km, and 2×10^{-4} gms/km for the 64 km/hr, one-hour cruise. This test does not distinguish between the above compounds. Because selenium is reputedly present on the filters, the general test procedure would be modified as described on pages 83-84 to eliminate the possibility of obtaining a false positive result for di- and tetravalent organic sulfur compounds.

A.4.3.2 Alkyl and Aromatic Sulfonic Acids

The test procedure used is described in pages 85-86 of Feigl The detection limits are about 2.5 μgms of material corresponding to a 1975 FTP emission rate of 1×10^{-3} gms/km, and 2.5×10^{-4} gms/km for the 64.36 km/hour, one-hour cruise. Sulfates do not interfere with the tests for sulfonic acids.

Table A-6 shows the averaged maximum emission rates based on chemical detection limits for both organic nitrogen and organic sulfur compounds.

TABLE A-6

ESTIMATED AVERAGE MAXIMUM EMISSION RATES (gms/km) AS DETERMINED BY DETECTION LIMIT OF SPOT TEST ON INDICATED VEHICLE TEST

Compound Type	1975 FTP	64 km/hr One-Hour Cruise
Organic Nitrogen	1×10^{-5}	2.5×10^{-6}
Compounds with Nitrogen and Oxygen Bonded Together	2×10^{-4}	5×10^{-5}
Aliphatic and Aromatic Nitro Compounds	3×10^{-4}	7.5×10^{-5}
Primary Aliphatic Nitro Compounds	2×10^{-4}	5×10^{-5}
Aromatic Nitro Compounds	6×10^{-4}	1.5×10^{-4}
Nitrates, Nitriles	1.2×10^{-4}	3×10^{-5}
Aliphatic and Aromatic Nitriles	4.4×10^{-3}	1.1×10^{-3}
Aliphatic Nitriles	4×10^{-3}	1×10^{-3}
Di- and Tetravalent Organic Sulfur Compounds	8×10^{-4}	2×10^{-4}
Alkyl and Aromatic Sulfonic Acids	1×10^{-3}	2.5×10^{-4}

A.5 Determination of Metallic Components of Exhaust Particulate

A.5.1 Emission Spectroscopy

A procedure was developed to measure the emission rate of the metals listed below by emission spectroscopy:

calcium, aluminum, zinc, chromium, iron, copper, nickel, lead.

Emission spectroscopy was chosen as the analytical technique not only because of its high sensitivity, but because it alone of the most various alternative analytical procedures considered, allows most of the metals to be measured by a single analytical procedure carried out on a single sample without resorting to separations.

Nickel and copper vehicular exhaust emissions have been determined in earlier work by differential pulse polarography(9). This technique is extremely sensitive and in many instances can measure metallic cations (in solution) in the ppb range. Differential pulse polarography could also be extended to measure exhaust chromium, iron, zinc and lead. Several sample preparations would be required however prior to polarographic analysis since some of the metal cations are best determined in alkaline medium, others in acidic medium, etc. In addition this technique cannot be used to determine calcium and aluminum, necessitating the use of two additional, and separate analytical procedures.

This spectrochemical method is based on the fact that all elements when vaporized and excited in an electric arc emit light energy at a series of wavelengths characteristic of that element. The emitted radiations for the sought for elements are separated by a grating, isolated and focused on the cathode of a photomultiplier. The photomultiplier transforms the radiant energy into electrical energy which is stored on a condenser of extremely low leakage rage. The charge on the condenser is related to the concentration by means of standard samples. This method has been in use at Exxon for some time in measuring trace metals in organic materials such as polymers and rubbers, and in a wide variety of materials such as slags, ashes, and minerals.

A.5.1.1 Preparation of Calibration Standards

Standards were prepared by spiking filters so that the levels for each metal ranged from 0.45 to 4.5 μgms/cm^2. The spiking solutions used were Matheson, Coleman and Bell Atomic Absorption 1000 ppm

Standard Solutions. A separate set of standards containing 4.5 to 11.25 μgms/cm^2 were prepared for Pb, Fe, and Zn, since it was found that the levels of these metals on the exhaust particulate filters frequently exceeded 4.5 μ gms/cm^2. Additional standards were prepared to simulate the combination of metals likely to be present on exhaust particulate filters. The surface concentrations of the metals in the mixture ranged from 0.45 to 4.5 μgms/cm^2. Samples high in Ni and Cu, but low in other metals were also prepared. In all cases, recovery was within ±15% of the quantity added to the filter. An ashless Millipore filter was used because of its high filtering efficiency, and negligible metals background.

Sample electrodes are prepared using the following reagents:

(1) Glycerol - U.S.P.

(2) Alcoholic $Mg(NO_3)_2 \cdot 6H_2O$

26.5 gm $Mg(NO_3)_2 \cdot 6H_2O$ 150 mg $CO(NO_3)_2 \cdot 6\ H_2O$	per liter of 95% Ethanol

(3) Aviation mix carbon

54 gm graphite
6 gm lithium carbonate

The electrode is prepared as follows:

The spiked 44 cm^2 Millipore filter is put into a 100 ml beaker, to which is added 1 ml of glycerol, 0.5 ml of magnesium nitrate solution, and 1 ml of concentrated sulfuric acid. The mixture is heated until the dense white fumes of SO_3 cease evolving. The sample is placed into a muffle furnace at 1000°F for one hour. This procedure is repeated if ashing was not complete the first time.

The ash is mixed with 400 ml of a 10% lithium carbonate, 90% carbon blend in a Wig L-Bug mixer, until a homogeneous mixture is obtained. This mixture is pressed into a 0.25 inch diameter electrode at 8000 PSI using an ARL power driven hydraulic briquetting press with a carbide lined mold assembly.

The finished pellet is inserted into a brace electrode holder in the quantometer, the counter electrode a 2-inch x 0.25-inch diameter, high purity graphite rod with a flat tip. The spectrometer used was a direct reading ARL Quantometer(10). The excitation source is a voltage spark of the ARL multi-source unit, Model No. 4700. High voltage excitation having the following parameters is used:

Primary Voltage	150
Discharges per cycle	4
Capacitance, μf	0.007
Inductance, μh	360

The exposure conditions are as follows;

Slit Width -	primary	20μ
	secondary	150μ
Prespark		10 seconds
Exposure		50 seconds

The 50-second exposure is controlled by a constant amount of energy from the internal standards.

The following analytical lines (A°), were used.

Element	A°
Li (Internal Standard)	6102
Ca	4303
Pb	2833
Cu	3274
Al	3944
Zn	3345
Cr	4254
Ni	3415
Fe	3021

Calibration curves are constructed by exciting the electrodes prepared from the calibration standards (described above) by plotting the spectral intensity versus concentration using linear coordinates. The low standard and high standard are used to set the instrument curve, and the curvature is established by the intermediate standards. Figures A-7 to A-15 show the calibration curves.

The spectral intensity obtained from the excitation of the electrodes from the samples are compared to those of the standards, and the equivalent μgm/cm^2 obtained from the calibration curves. The emission rate (ER) in gms/km of a given metal is obtained as follows:

$$\text{ER in gms/km} = \frac{(\mu\text{gms/cm}^2) \times 10^{-6}\ \text{gms}/\mu\text{gm} \times \text{Filter Area}}{(\Delta\text{km})\ F}$$

where Δkm is the distance in kilometers accumulated on the test and F is the probe volume fraction sampling rate.

Figure A-7

Calibration Curve for Nickel

150 Volts, ~45 Second Burning Time

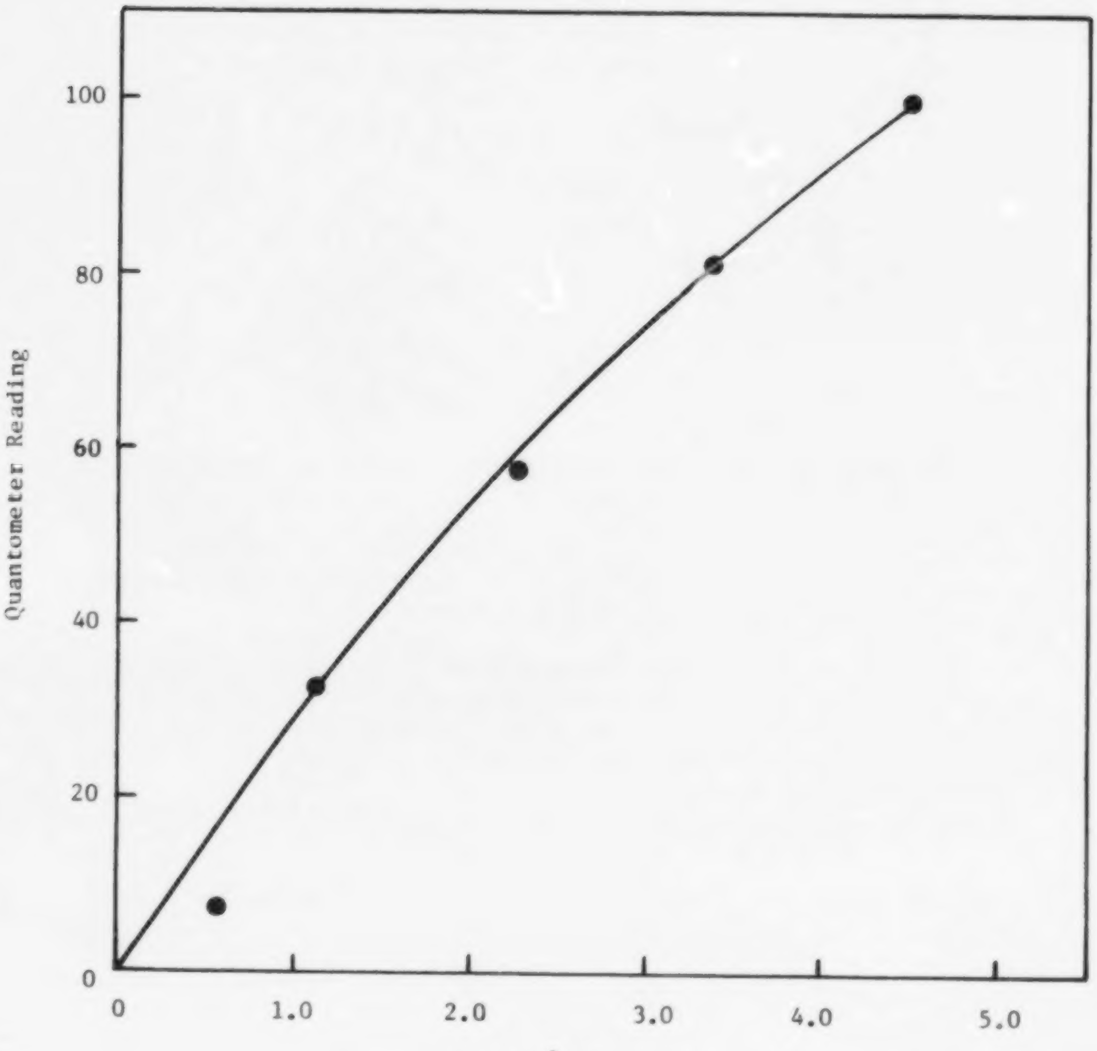


Figure A-8

Calibration Curve for Aluminum

150 Volts, $\simeq$45 Second Burn Time

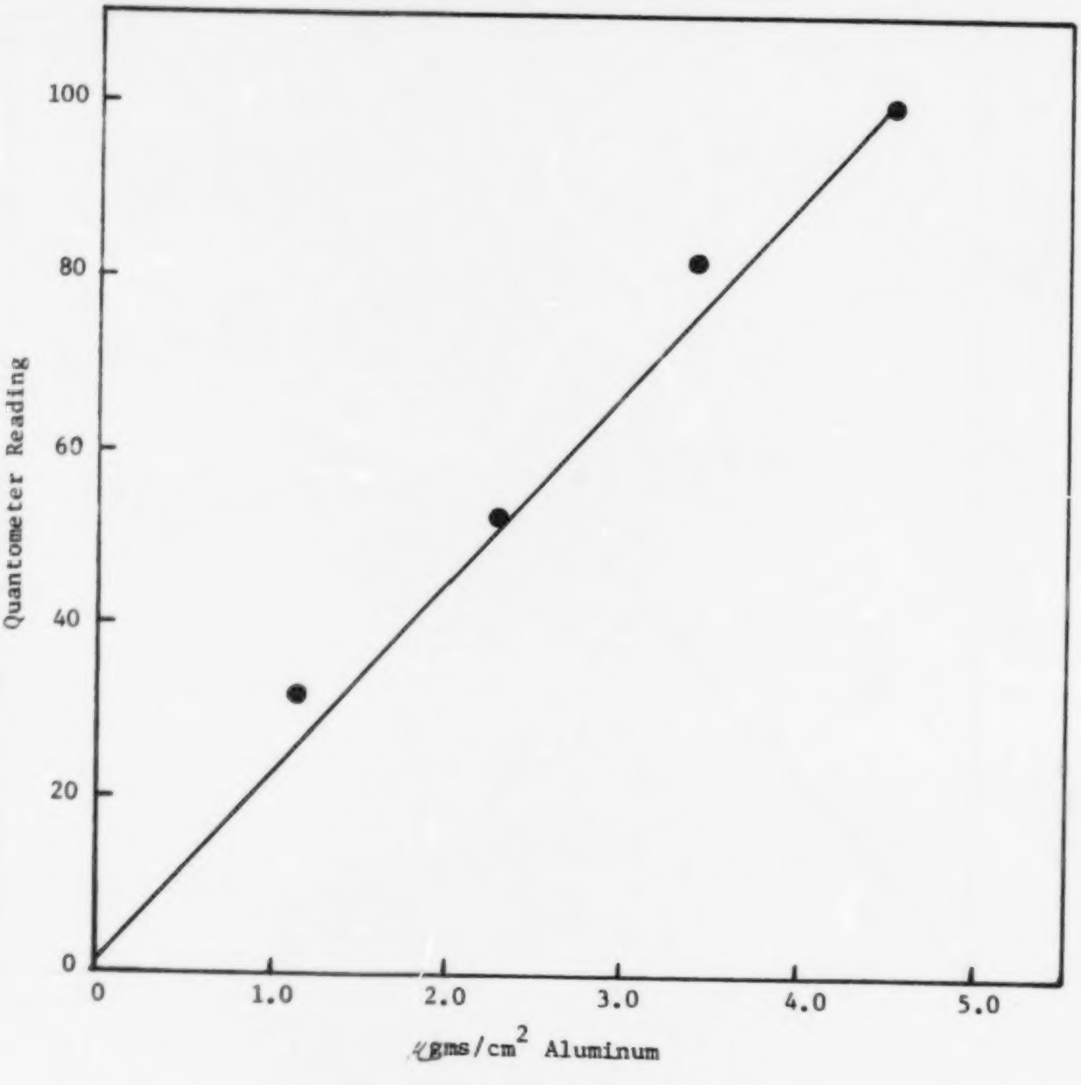


Figure A-9

Calibration Curve for Calcium

150 Volts, ~45 Second Burn Time

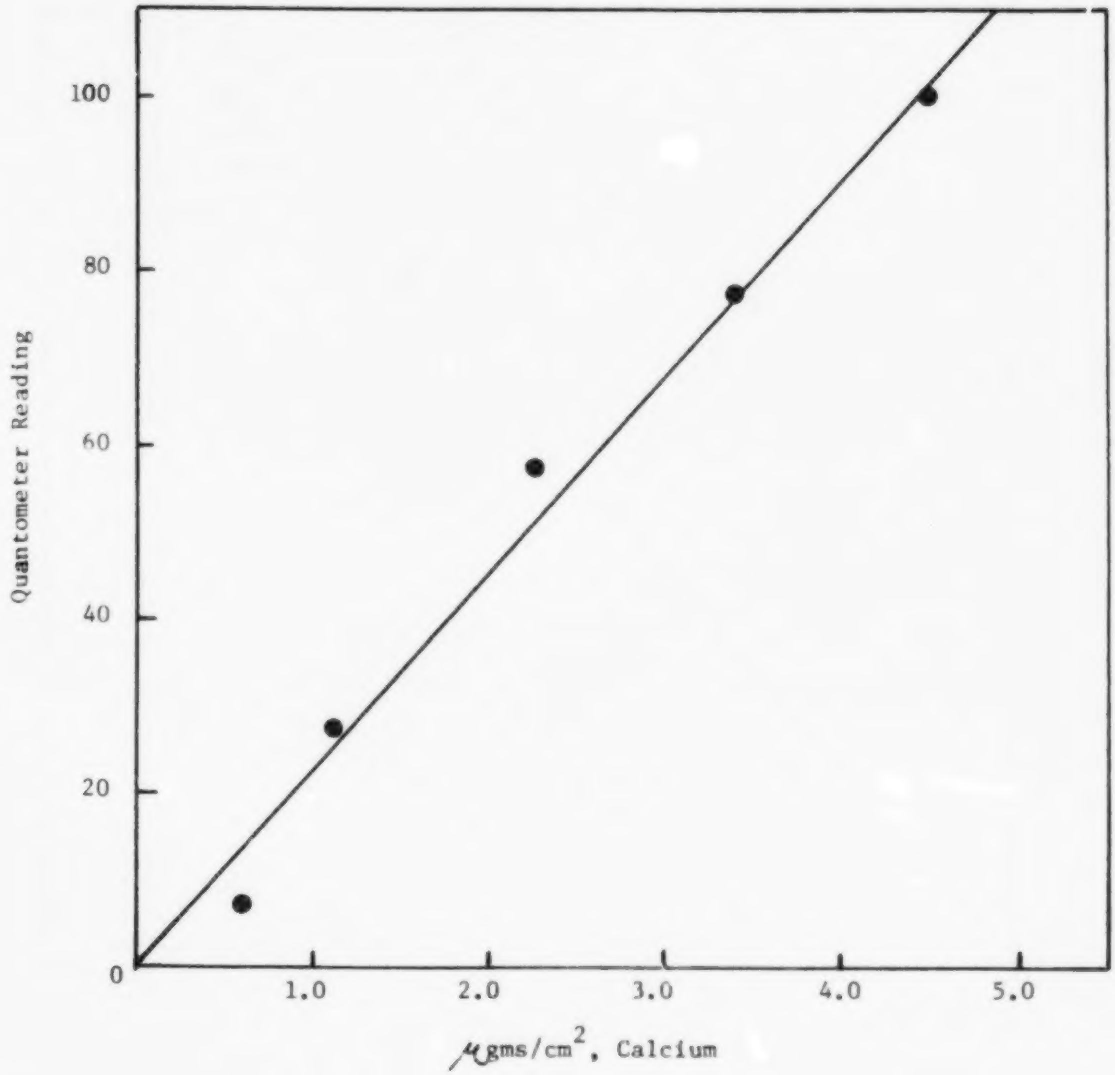


Figure A-10

Calibration Curve for Copper

150 Volts, ~45 Second Burn Time

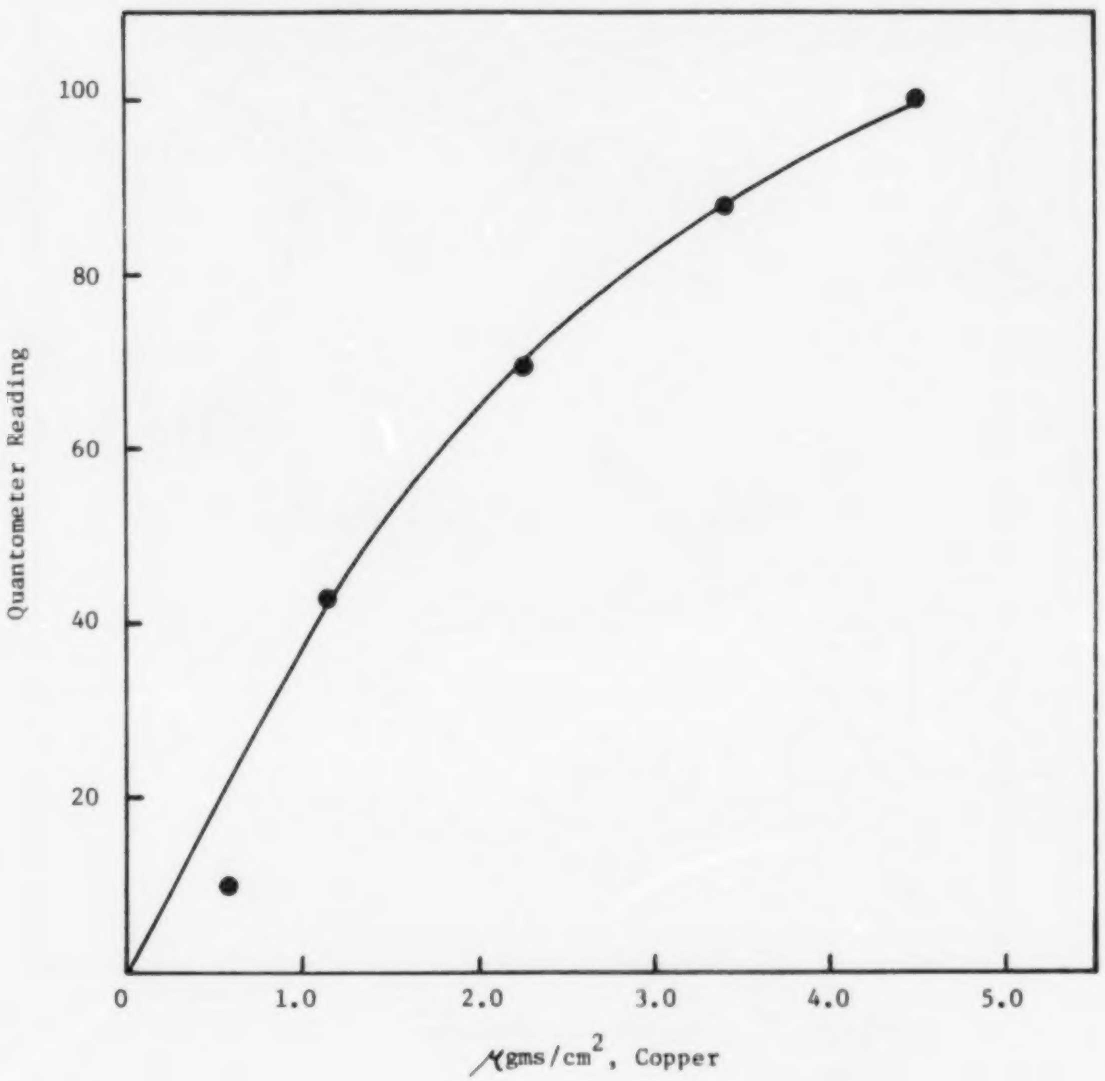


Figure A-11

Calibration Curve for Chromium

150 Volts, ≃45 Second Burn Time

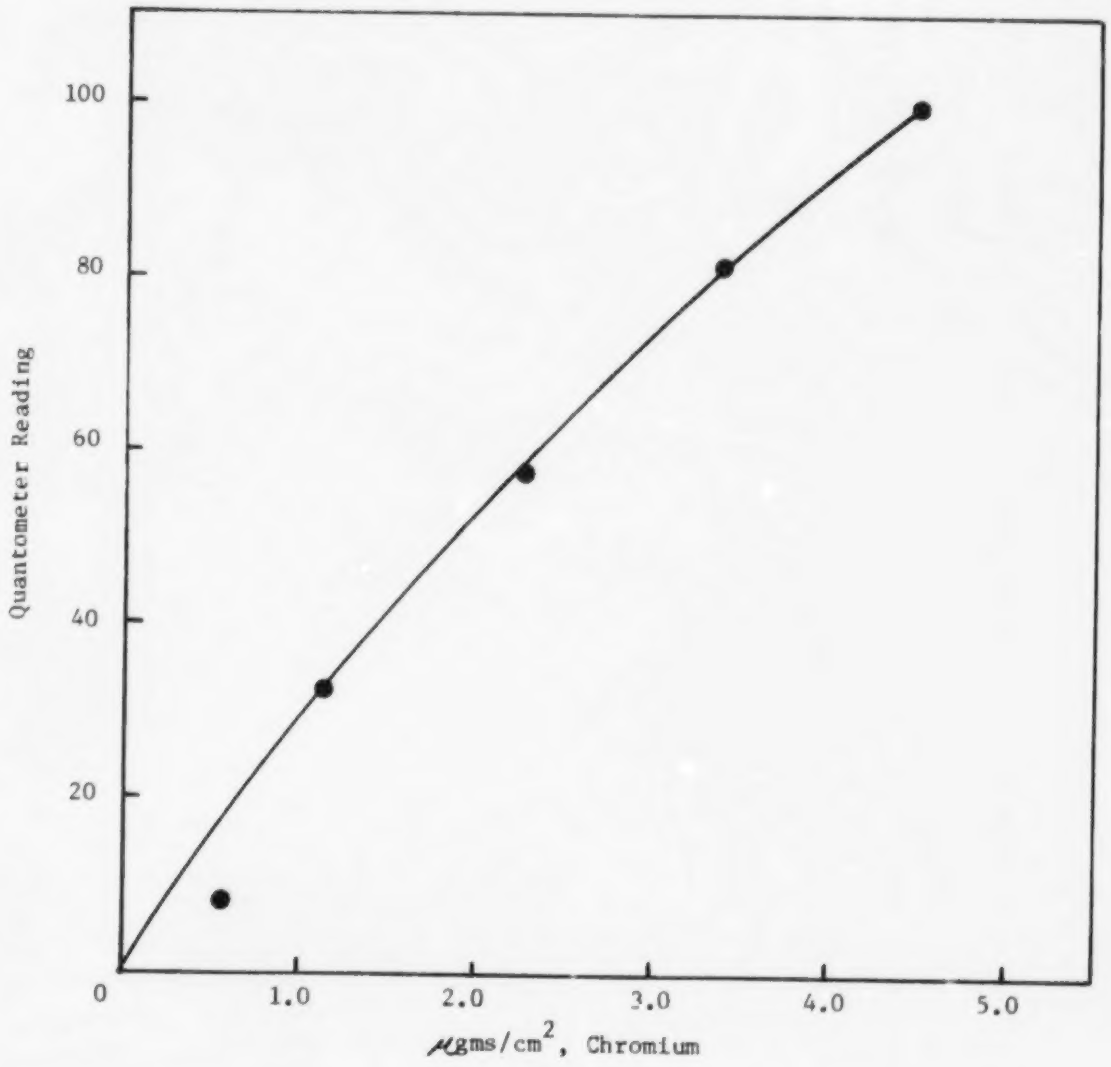


Figure A-12

Calibration Curve for Zinc

150 Volts, ~45 Second Burn Time

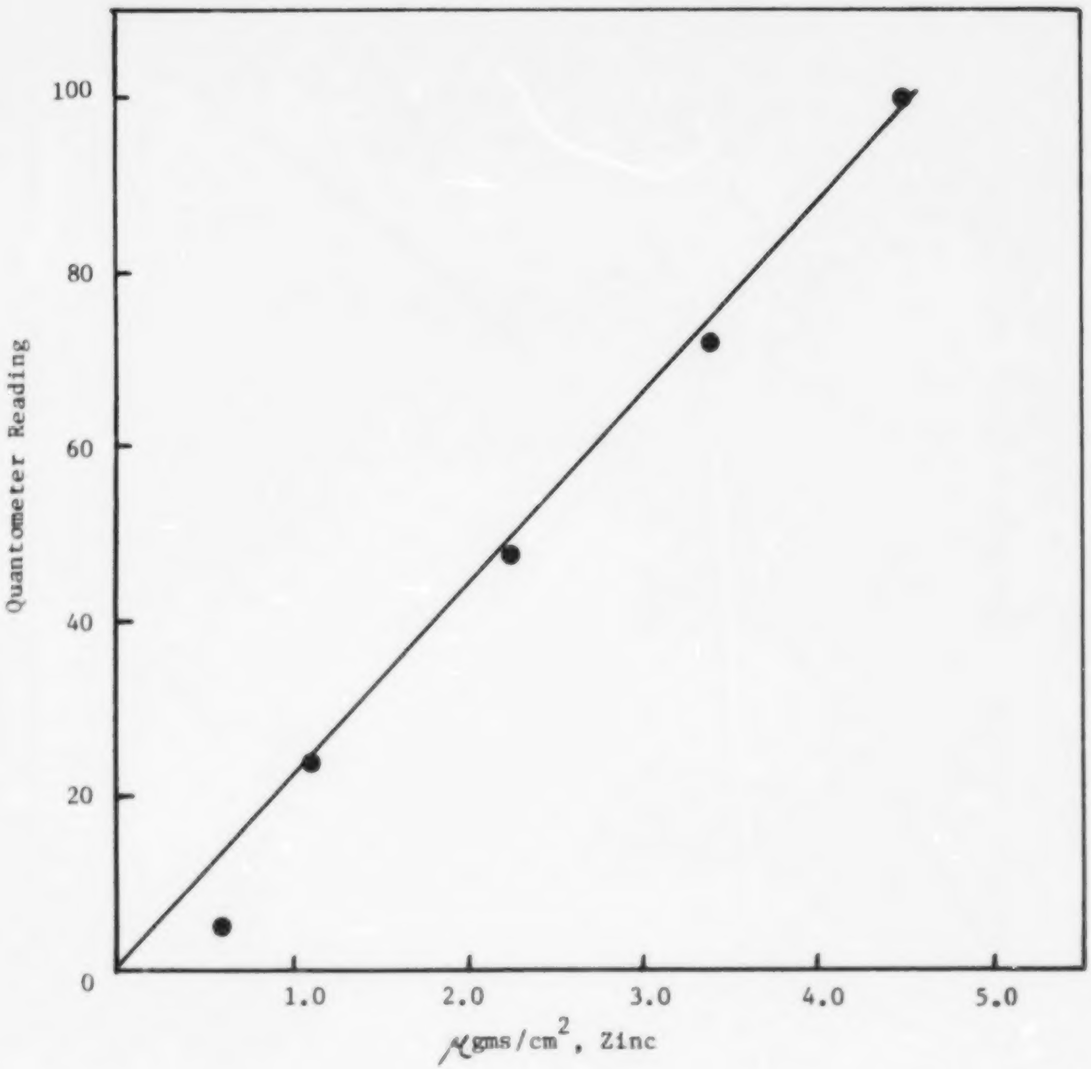


Figure A-13

Calibration Curve for Lead

150 Volts, ~45 Second Burn Time

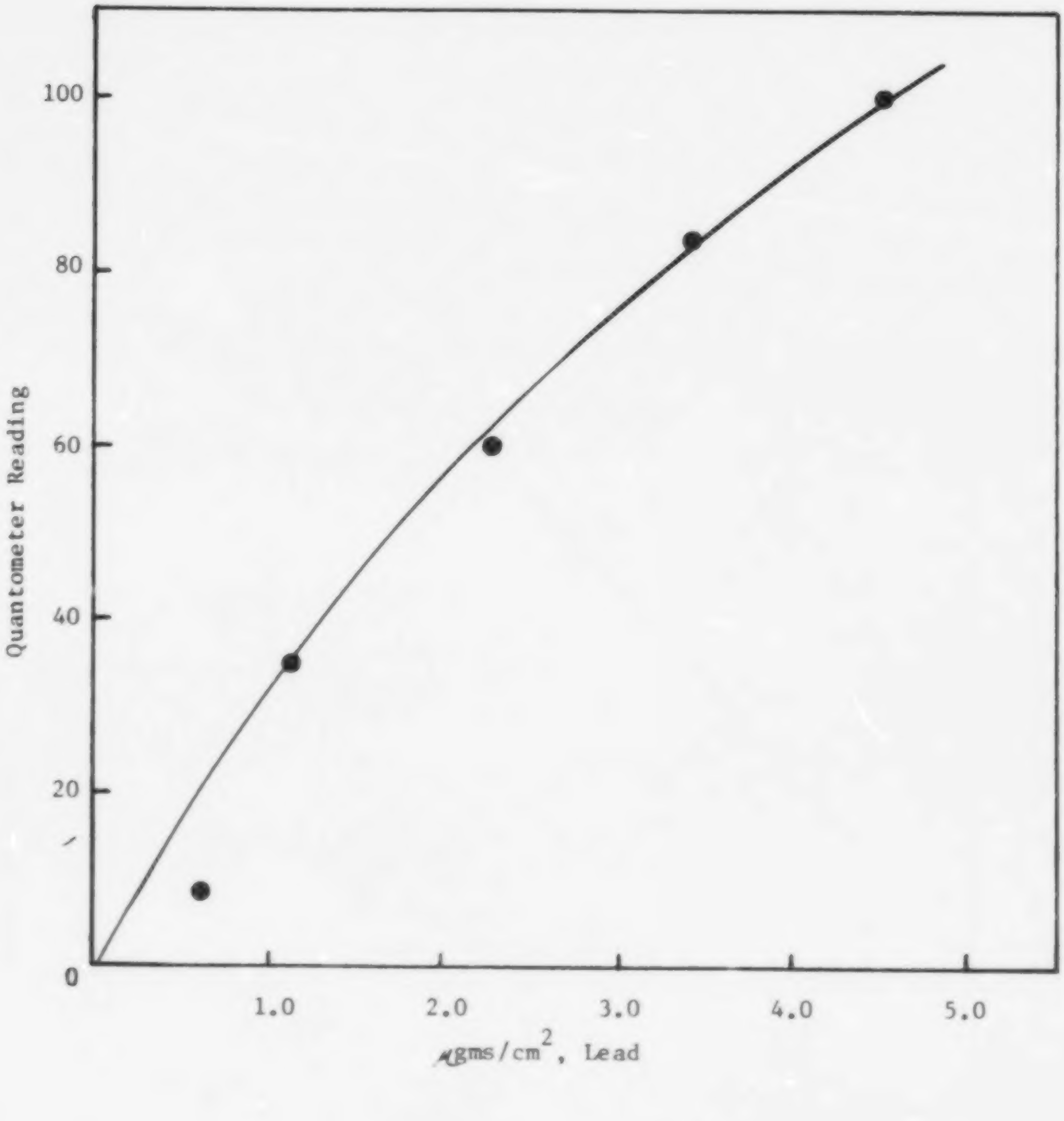


Figure A-14

Calibration Curve for Iron

150 Volts, ≃45 Second Burn Time

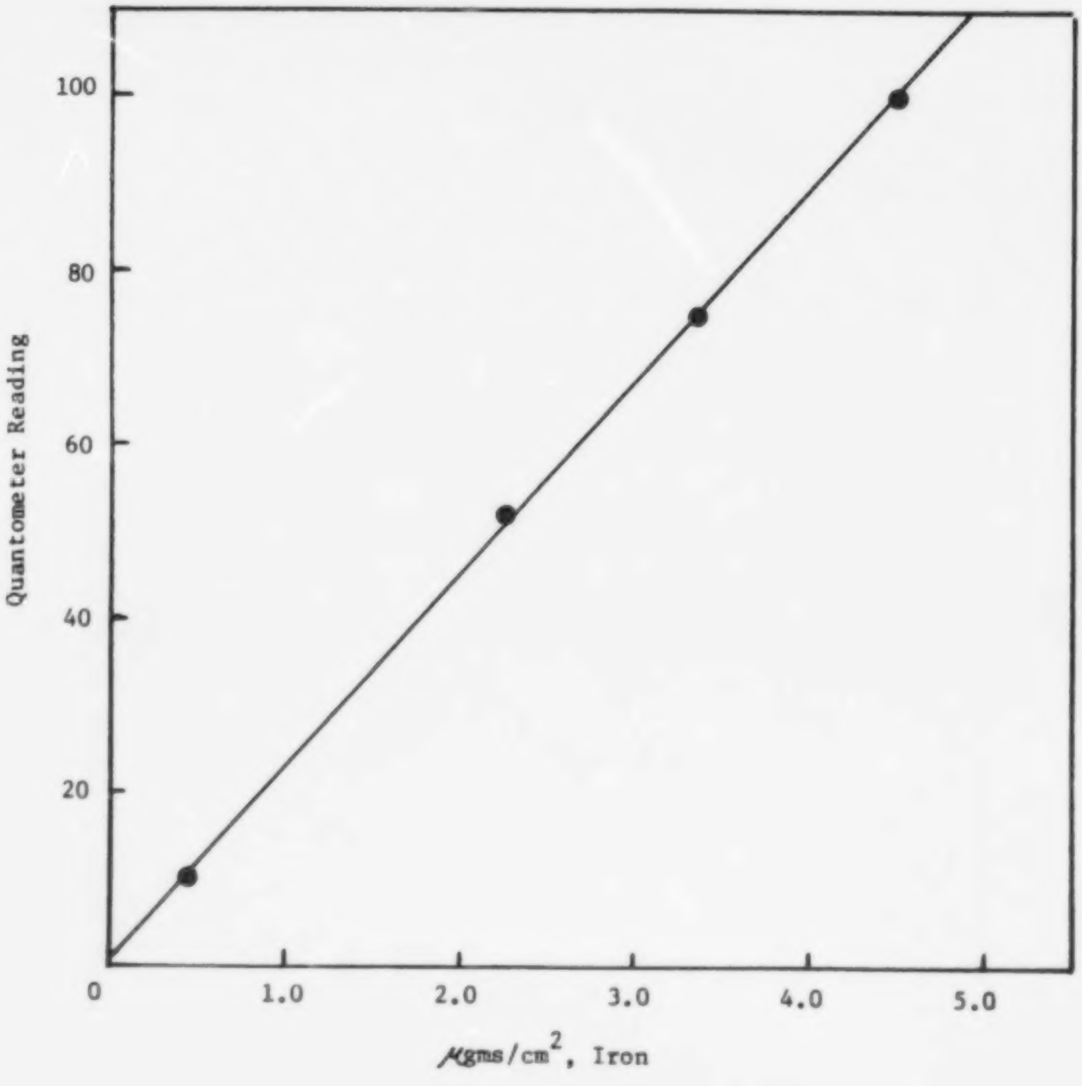
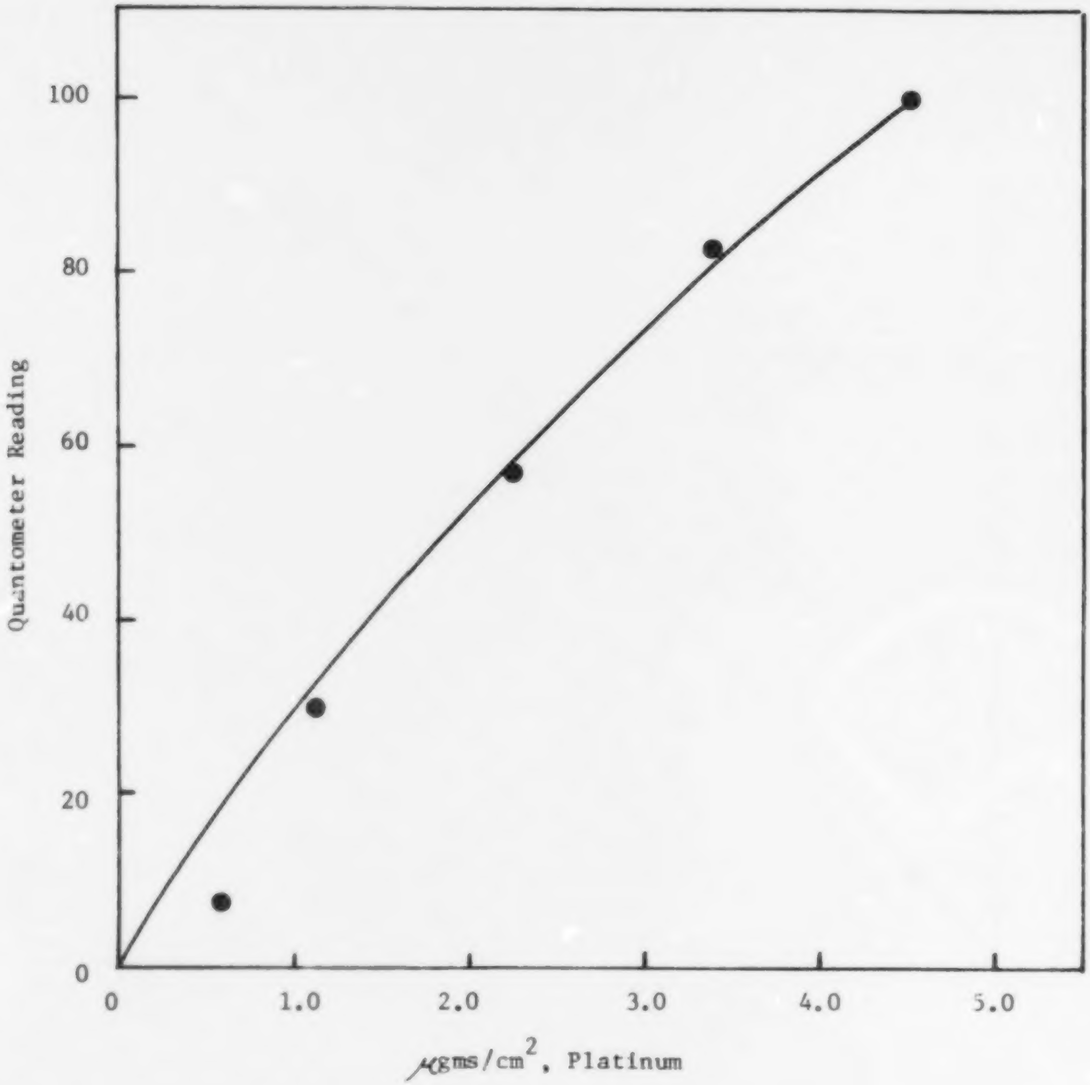


Figure A-15

Calibration Curve for Platinum

150 Volts, ~45 Second Burn Time



A.5.1.2 Assessment of Interaction Effects on Metal Determinations

Since filters from vehicle test runs would invariably have a combination of various metals or metal derived particulate matter, it was necessary to determine if there were any interactions which produced interference which invalidated the 0.45 to 4.5 μgm/cm^2 calibration curves for any or all of the metal containing components.

Measurements were made with filters spiked with salts of Ca, Pb, Fe, Cu, Al, Zn, Cu, Ni, and Pt to ascertain if major interferences exist. The results (excluding Pt) are shown below in Table A-7. In some of the mixtures several of the components were present at levels below the minimum detection limit, and above the upper calibration limit.

This test matrix had a two-fold purpose:

(1) To determine if spurious results for some metals would be obtained because of high levels of other metal components.

(2) To determine if the presence of other metals would produce interactions such that metals which were present at levels above and/or below the calibration limits would appear to be at levels within the calibration limits.

Table A-7 shows that there are no major interferences so that each of the metals or their salts may be determined in the presence of the others without a major error. The average recovery for each metal within the calibration limits is about 86%.

Regression analysis for each of the metals showed:

$$(1)\ \frac{\mu\mathrm{gms}}{\mathrm{cm}^2}\ \mathrm{Ca\ (found)} = 0.88\ \frac{\mu\mathrm{gms}}{\mathrm{cm}^2}\ \mathrm{Ca\ (present)} + 0.08\ \mu\mathrm{gms/cm}^2$$

$$(2)\ \frac{\mu\mathrm{gms}}{\mathrm{cm2}}\ \mathrm{Al\ (gound)} = 0.97\ \frac{\mu\mathrm{gms}}{\mathrm{cm}^2}\ \mathrm{Al\ (present)} - 0.07\ \mu\mathrm{gms/cm}^2$$

$$(3)\ \frac{\mu\mathrm{gms}}{\mathrm{cm2}}\ \mathrm{Fe\ (found)} = 0.83\ \frac{\mu\mathrm{gms}}{\mathrm{cm}^2}\ \mathrm{Fe\ (present)} - 0.35\ \mu\mathrm{gms/cm}^2$$

$$(4)\ \frac{\mu\mathrm{gms}}{\mathrm{cm}^2}\ \mathrm{Cu\ (found)} = 0.93\ \frac{\mu\mathrm{gms}}{\mathrm{cm}^2}\ \mathrm{Cu\ (present)} + 0.09\ \mu\mathrm{gms/cm}^2$$

$$(5)\ \frac{\mu\mathrm{gms}}{\mathrm{cm}^2}\ \mathrm{Pb\ (found)} = 1.01\ \frac{\mu\mathrm{gms}}{\mathrm{cm}^2}\ \mathrm{Pb\ (present)} - 0.039\ \mu\mathrm{gms/cm}^2$$

(6) $\frac{\mu gms}{cm^2}$ Zn (found) = 0.93 $\frac{\mu gms}{cm^2}$ Zn (present) + 0.129 $\mu gms/cm^2$

(7) $\frac{\mu gms}{cm^2}$ Cr (found) = 0.89 $\frac{\mu gms}{cm^2}$ Cr (present) - 0.120 $\mu gms/cm^2$

(8) $\frac{\mu gms}{cm^2}$ Ni (found) = 0.85 $\frac{\mu gms}{cm^2}$ Ni (present) + 0.05 $\mu gms/cm^2$

Regression analysis for the eight metals showed:

$\frac{\mu gms}{cm^2}$ (any metal found) = 0.91 $\frac{\mu gms}{cm^2}$ (any metal present) + 0.07 $\frac{\mu gms}{cm^2}$

A.5.1.3 Effect of Presence of Chromium on Platinum Determination

It was shown however, that although platinum could be determined by emission spectroscopy to the same sensitivity levels as the other metals (Figure A-15), the presence of chromium causes appreciable positive deviations for platinum. Table A-8 summarizes the experimental matrix which demonstrates the interference for platinum by chromium.

Even though the sample contains no platinum, the quantometer indicates that platinum would be present. Table A-8 shows that it is the chromium which is responsible for the spurious platinum readings. The platinum readings on the quantometer were essentially constant for the same quantity of chromium despite a four-fold change in the nickel level and a ten-fold change in the copper level. Figure A-16 shows that the false quantometer readings for platinum vary linearly with the quantity of chromium present, but is not a function of other metals such as nickel and copper. Platinum therefore was not determined by emission spectroscopy, but by X-ray fluorescence. This method is discussed in Section A.5.2 of this Appendix.

A.5.1.4 Calibrations for High Levels of Iron, Zinc and Lead

In the course of carrying out the program it was found that iron, zinc, and lead, were frequently found at levels above 4.5 μgms/cm^2. Additional calibrations for these three metals were made at filter loadings up to 11.25 μgms/cm^2. The higher loading calibration curves for these metals are shown in Figures A-17 to A-19.

A.5.2 Platinum Analysis by X-ray Fluorescence

Platinum analysis on the glass fiber filters was performed by X-ray fluorescence, since it was found that chromium interfered with the determination of platinum when using emission spectroscopy.

Figure A-16

False Platinum Response of Quantometer Due to Presence of Chromium

150 Volts, ~45 Second Burn Time

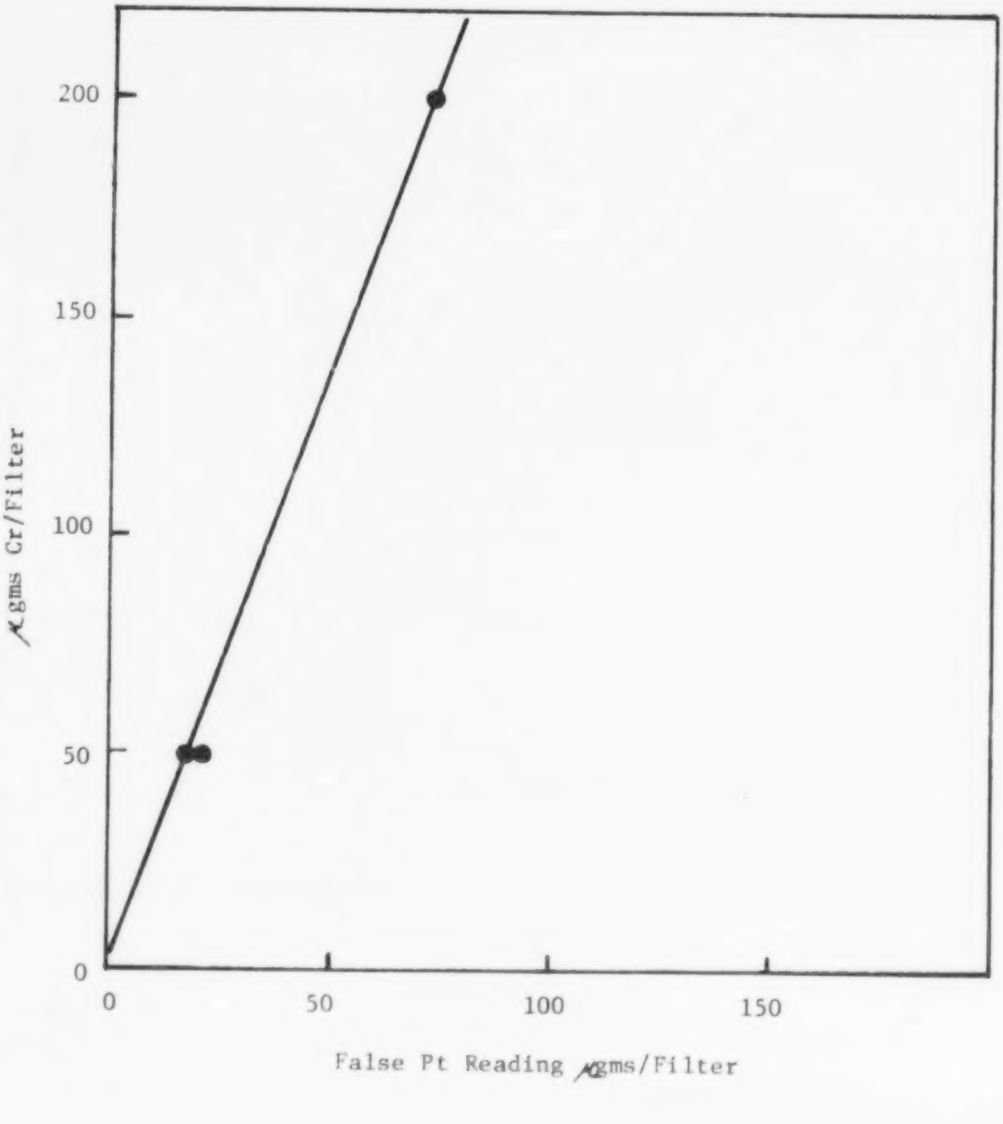


Figure A-17

Calibration Curve for Lead
(4.5 to 11.25 μgms/cm^2)

150 Volts, ≃45 Second Burn Time

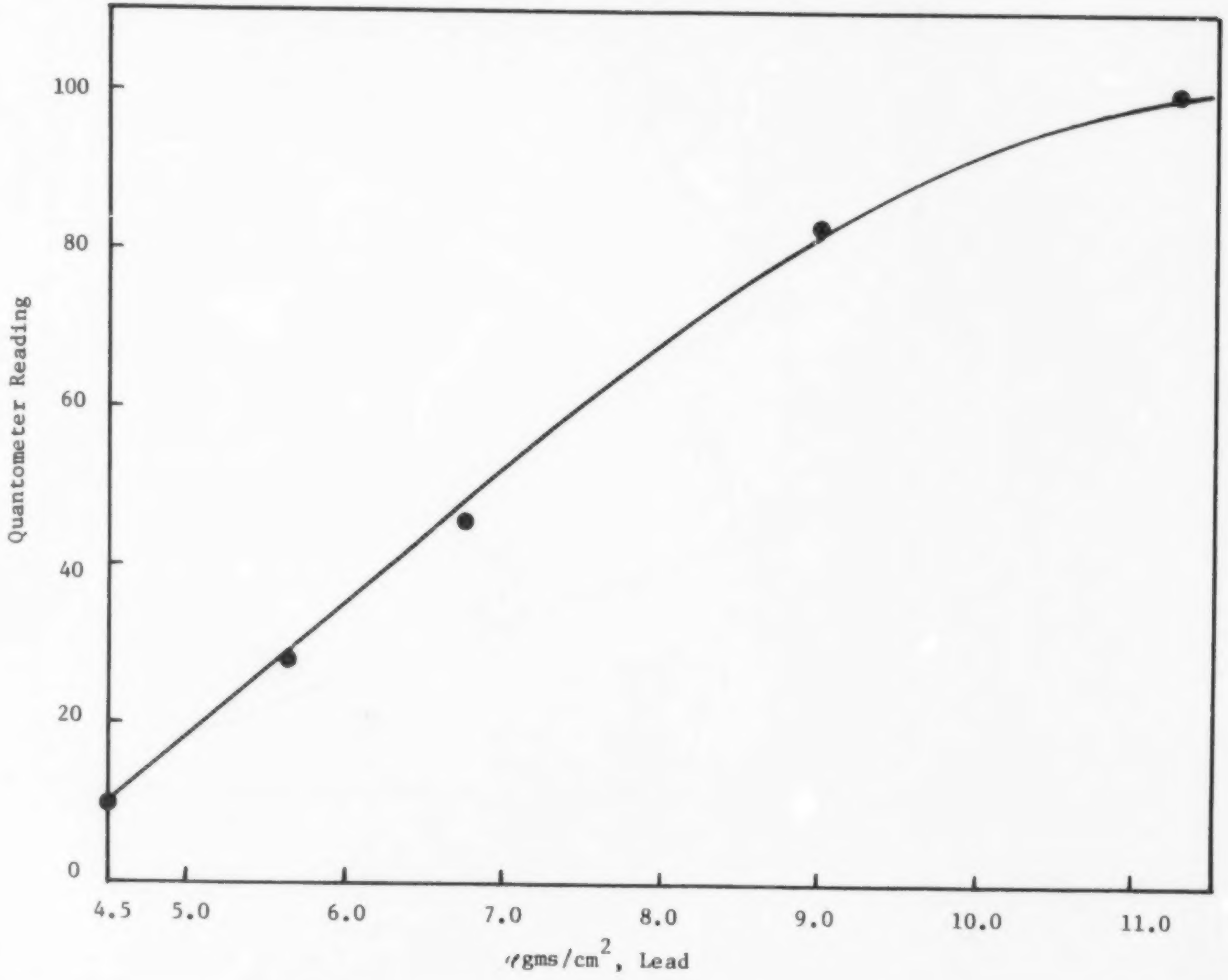


Figure A- 18

Calibration Curve for Iron
(4.5 to 11.25 μgms/cm^2)

150 Volts, $\simeq$45 Second Burn Time

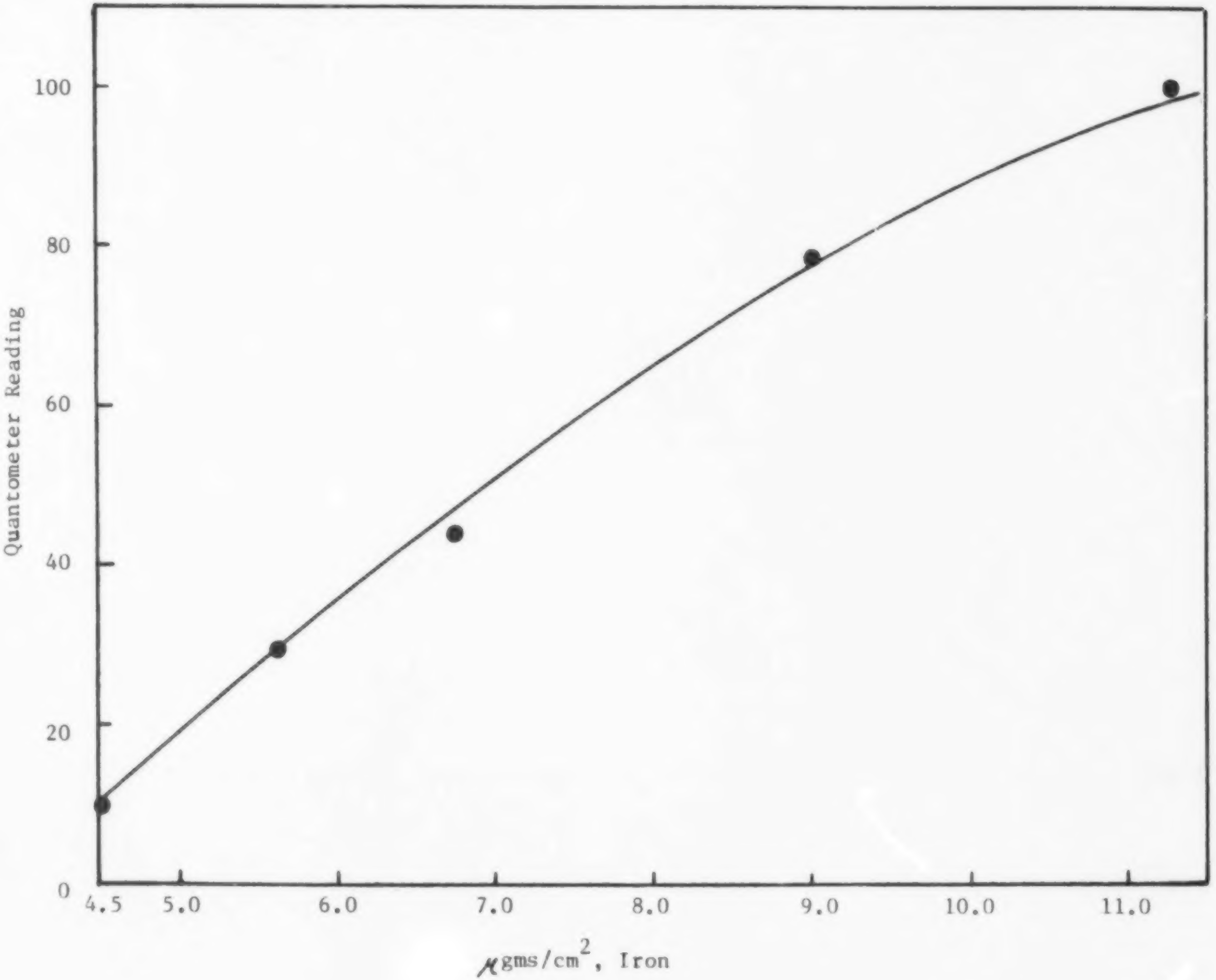


Figure A-19

Calibration Curve for Zinc
(4.5 to 11.25 µgms/cm^2)

150 Volts, ~45 Second Burn Time

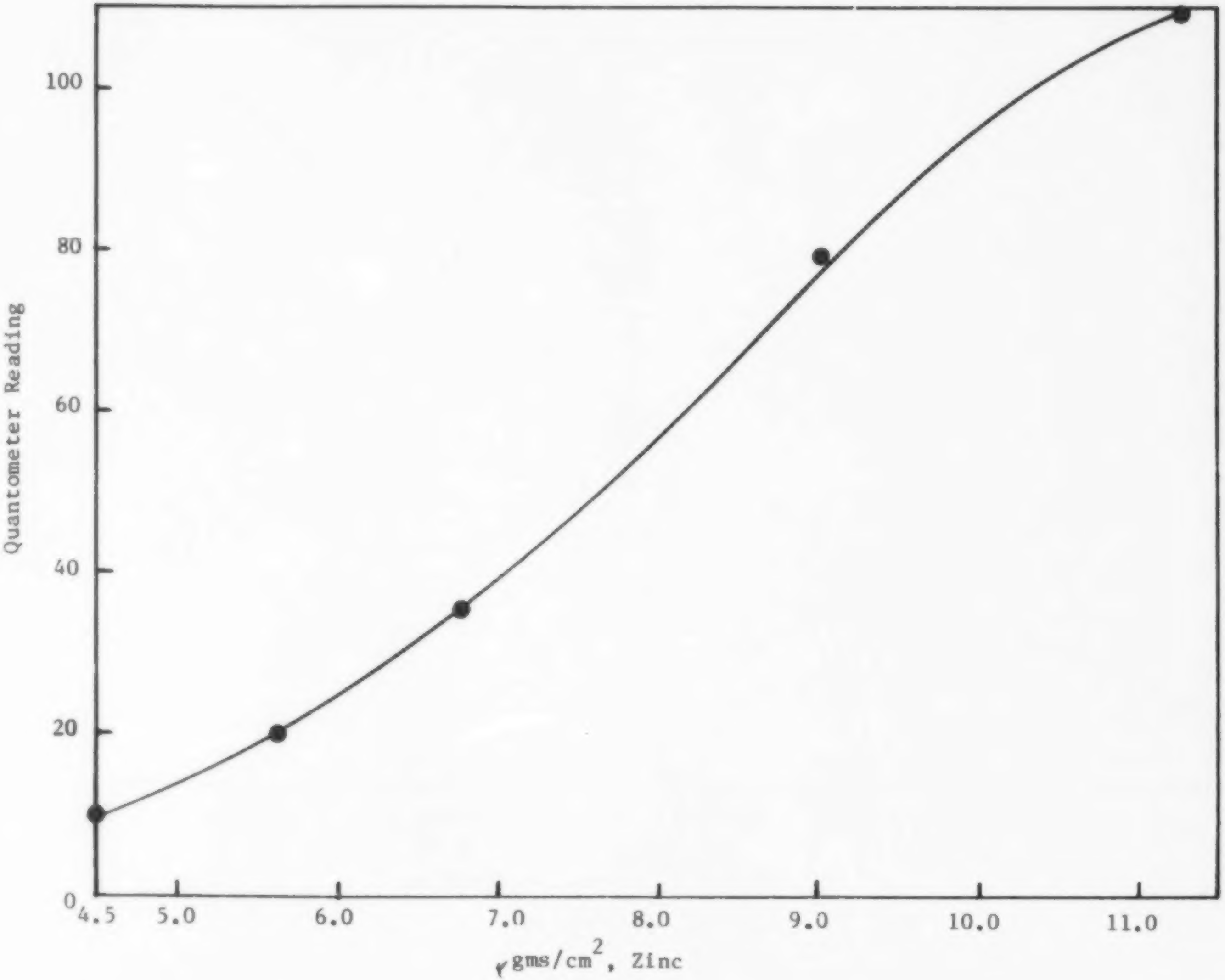


TABLE A-7

EFFECTS OF PRESENCE OF OTHER METALS ON DETERMINATION OF A SELECTED METAL (0.45 to 4.5 µgm/cm^2 CALIBRATION CURVE)

	Metals Determined							
	Ca	Pb	Fe	Cu	Al	Zn	Cr	Ni
µgms/cm^2 added	0.25	0.51	0.51	0.25	0.25	0.25	0.25	0.25
µgms/cm^2 found	<0.45	0.45	0.70	<0.45	<0.45	<0.45	<0.45	<0.45
Percent Recovery	(a)*	88	137	(a)	(a)	(a)	(a)	(a)
µgms/cm^2 added	1.01	1.01	2.02	1.01	1.01	1.01	1.01	1.01
µgms/cm^2 found	1.00	1.20	2.10	1.05	1.05	1.15	1.05	1.05
Percent Recovery	99	119	104	104	104	114	104	104
µgms/cm^2 added	1.52	2.02	4.05	1.52	1.52	4.05	1.52	1.52
µgms/cm^2 found	1.65	2.30	4.00	1.60	1.65	4.40	1.65	1.45
Percent Recovery	109	114	99	105	109	109	109	95
µgms/cm^2 added	2.02	2.53	5.06	2.02	2.02	2.02	2.02	2.02
µgms/cm^2 found	1.65	2.35	4.25	1.80	1.80	1.90	1.85	1.65
Percent Recovery	82	93	84	89	89	94	92	82
µgms/cm^2 added	2.53	3.54	6.58	2.53	2.53	3.04	2.53	2.53
µgms/cm^2 found	2.35	3.60	>4.50	2.45	2.50	2.95	2.45	2.20
Percent Recovery	93	102	(a)	97	99	97	97	87
µgms/cm^2 added	3.04	5.06	7.59	3.04	3.04	5.06	3.04	3.04
µgms/cm^2 found	2.60	>4.50	>4.50	2.80	2.80	4.30	2.75	2.45
Percent Recovery	84	(a)	(a)	92	92	85	90	81
µgms/cm^2 added	3.54	7.59	9.11	3.54	3.54	7.59	3.54	3.54
µgms/cm^2 found	3.15	>4.50	>4.50	3.40	3.35	>4.50	3.30	3.05
Percent Recovery	89	(a)	(a)	96	95	(a)	93	86
µgms/cm^2 added	4.05	8.60	10.12	4.05	4.05	10.63	4.05	4.05
µgms/cm^2 found	3.90	>4.50	>4.50	3.90	3.95	>4.50	3.90	3.65
Percent Recovery	96	(a)	(a)	96	98	(a)	96	90
µgms/cm^2 added	4.55	10.63	11.64	4.55	4.55	11.64	4.55	4.55
µgms/cm^2 found	3.85	>4.50	>4.50	4.25	3.90	>4.50	3.95	3.85
Percent Recovery	85	(a)	(a)	93	86	(a)	87	85
µgms/cm^2 added	0.51	13.16	13.16	0.25	0.51	13.16	0.51	0.51
µgms/cm^2 found	0.50	>4.50	>4.50	<0.45	0.45	>4.50	<0.45	<0.45
Percent Recovery	98	(a)	(a)	(a)	88	(a)	~88	88

*(a) The metal loading was either above the upper calibration limit (4.5 µgms/cm^2) or below the detection limit (0.45 µgms/cm^2). In all cases where the metal loading were beyond the calibration limits, the measurements correctly indicated this to be the case.

TABLE A-8

PLATINUM-CHROMIUM INTERFERENCE

Micrograms of Indicated Metal in Sample				Quantometer Readings for Indicated Metal							
Pt	Ni	Cr	Cu	Pt	Pb	Cu	Al	Zn	Cr	Ni	Ca
0	0	0	0	0	--	--	--	--	--	--	--
50	0	0	0	25.5	--	--	--	--	--	--	--
200	0	0	0	100.0	--	--	--	--	--	--	--
0	0	50	0	17.0	--	--	--	--	32.0	--	--
0	0	200	0	71.0	--	--	--	--	95.5	--	--
0	200	50	50	19.5	0.0	40.5	-3.0	0	35.0	89.5	5.5
0	50	50	5	17.5	0.0	4.0	-4.0	0	32.5	27.0	4.0

The X-ray procedure involves exposing circular sections of the exhaust particulate filter in the X-ray beam of a Phillips Number 1220 X-ray spectrometer. An internal standard is made by spiking one of these filters with 40 μgm of platinum as an aqueous solution. The platinum X-ray peak intensity of the two filters is then compared and the platinum content of the sample filter determined. Blank filters are run in every determination. The minimum detectable level of platinum by this technique is about 0.35 μgm/cm^2

The maximum possible emission rates based on this sensitivity limit is:

5.6×10^{-5} gms/km for the 1975 FTP

and 1.55×10^{-5} gms/km for the 64.36 km/hr, one-hour cruise

APPENDIX B

MODIFIED ANDERSEN IMPACTOR

A model 0203 Anderson Impactor was modified and adapted for use withdrawing samples from the dilution tunnel. Sampling of the usual 1 CFM however meant that the opening of the sampling probe coupled to the impactor would be only 5mm when sized to the flow development tunnel. A probe opening this small is conducive to material sampling losses in the probe. The recommended minimum probe diameter to prevent these losses is 6.4mm(11). Increasing the volumetric flow rate through the impactor would allow longer probe openings to be used. However, the high pressure drop through the impactor limits the volumetric flow rates and, therefore, the probe dimensions that can be used in the flow development tunnel.

As a compromise, the flow rate used for sampling with the impactor is 1.5 CFM corresponding to a probe opening consistent with isokinetic sampling of 6.4MM. The probe was flared up to one inch ID, a half inch beyond the probe opening. This probe was bent at right angles in the tunnel so that it emerged from the tunnel bottom. It was necessary to do this because there was insufficient space for the impactor to fit in with the filter housings at the tunnel end.

To obtain size distributions by weight, one mil thick stainless steel shimstocks replaced the particulate collection plates normally used in the Andersen Impactor. The standard collection plates weigh about 20 grams, which exceeds the 10 gram capacity of the Mettler microbalance used for weighing. The shimstock was washed progressively in cyclohexane-toluene mixture, alcohol, acetone, and then cleaned ultrasonically in an aqueous detergent solution. The shimstock was then rinsed with distilled water to remove the detergent, successively washed in alcohol and acetone and then dried.

The cleaned shimstocks were kept in Petri dishes in a constant temperature - constant humidity room and weighed daily for four days. Expensive testing indicated that the weight change that would be incurred by a shimstock during a vehicle run should be a reliable measure of the weight of material deposited of a given particle size range. The average weight variation of a clean unused shimstock over a four day interval was only ± 8ugms.

Several tests were carried out under 64.km/hr and 96.km/hr cruises using an oxidation catalyst equipped vehicle operating on a 0.046 wt % sulfur fuel. These test conditions were chosen to determine the feasibility of the modified impactor. Steady state cruises with a catalyst equipped vehicle should allow sufficient material to be collected on the Impactor stages to obtain a size distribution by weight. The total particulate emission rates obtained with the impactor should be in agreement with those obtained from the parallel total filters. Lack of agreement between the total particulate emissions obtained with the Impactor and the total filters would mean that the Impactor modifications interferred with its functioning properly.

All seven stages of the Impactor were used for these test runs, as was the absolute filter. This filter is from the same batch as the 15CFM filters (Gelman Type A Glass Fiber Filter). The results for each of the runs in terms of total particulate emissions and sulfuric acid emissions is shown in Tables B-1 and B-2.

TABLE B-1
Comparison of Impactor and Total Filters

64 km/hr, (40mph), one hour cruise vehicle
equipped with PTX-IIB oxidation catalyst
Fuel Sulfur, 0.046 wt. %

Particulate Type	Particulate Emission Rate gms/km Modified Impactor	Total Filters (1)	Total Filters (2)
Total	0.080	0.087	0.087
Sulfate	0.034	0.034	0.033

The agreement between the Impactor and the total filters is within 5% for both total particulate and sulfate emissions. About 90% of the particulate and all of the sulfate was less than one micron as shown below.

TABLE B-2
Distribution of Particulate in
Modified Anderson Impactor
gms/km

Particulate Type	Sum of Shims (1-7)	Absolute Filter	Shims plus Filter
Total	0.009	0.071	0.080
Sulfate	(not detected)	0.034	0.034

As shown in Figure B-1, the particulates above one micron were log normally distributed. Similar results were obtained with the 96 km/hr (60 mph) one hour cruise as shown in Table B-3.

FIGURE B-1

OXIDATION CATALYST
EQUIPPED VEHICLE

0.046% S FUEL

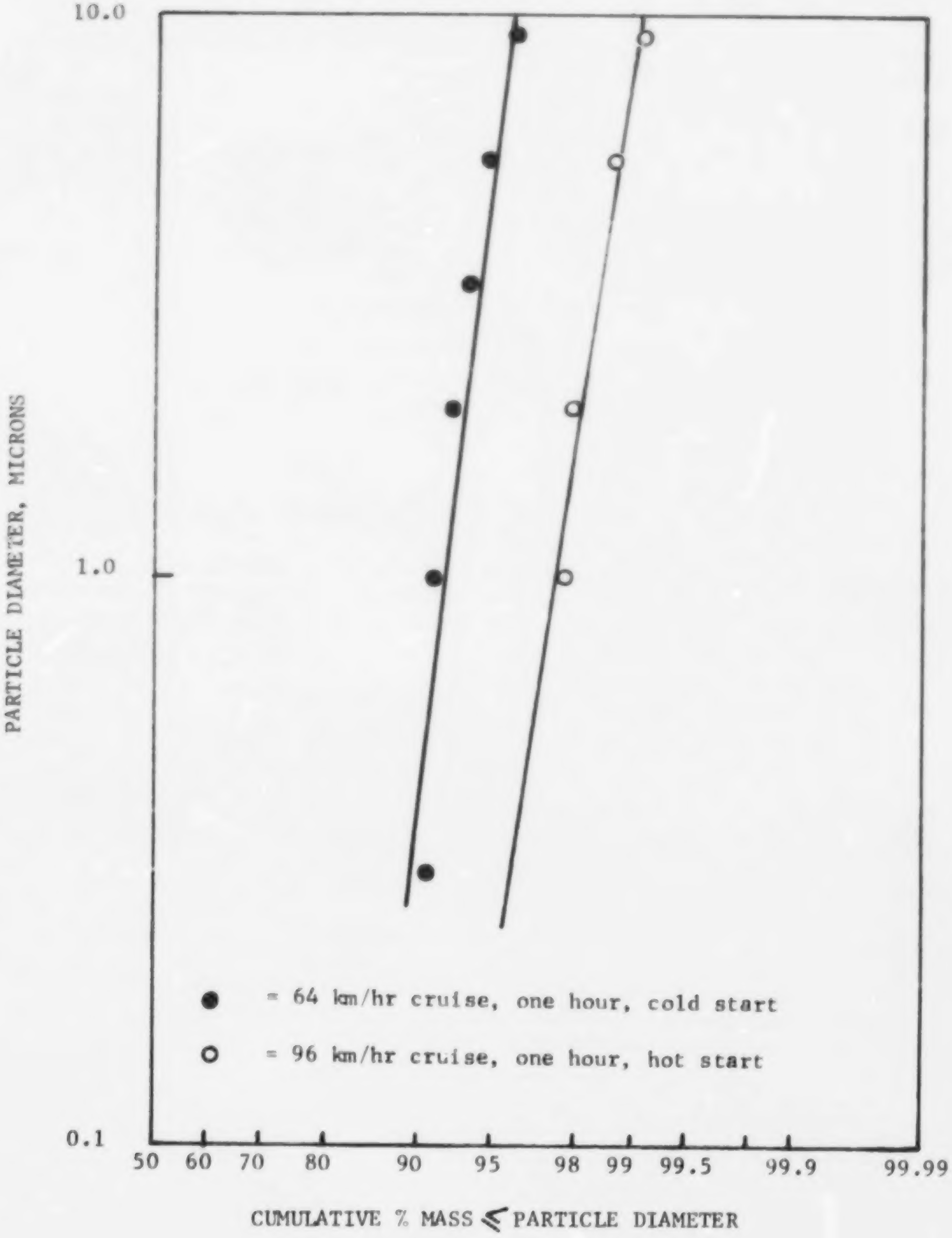


TABLE B-3
Comparison of Impactor and Total Filters

96 km/hr (40mph) one hour cruise vehicle equipped with PTX-IIB oxidation catalyst - Fuel Sulfur, 0.046 wt. %

Particulate Emission Rate gms/km

Particulate Type	Modified Impactor	Total Filters (1)	(2)
Total	0.128	0.130	0.131
Sulfate	0.060	0.055	0.053

Again good agreement between the Impactor and total filters is obtained with respect to total particulate and sulfate emissions is obtained.

Over 95% of the total particulate and effectively all of the sulfate is less than one micron in diameter as shown in Table B-4.

TABLE B-4
Distribution of Particulate in Modified Andersen Impactor (96.54 km/hr cruise) gms/km

Particulate Type	Sum of Shims (1-7)	Absolute Filter	Shims plus Filter
Total	0.004	0.124	0.128
Sulfate	(not detected)	0.060	0.060

As in the previous case, the particulates greater than one micron in diameter were log normally distributed, Figure B-1. Thus, it appears that at least for type of steady state cruises in which the particulate emissions are high, the data obtained with the modified Impactor are reliable. It was found that the particulate matter on the shimstocks was difficult to remove. Accordingly, new shimstocks were used for each run.

APPENDIX C

EXHAUST SPLITTER

An exhaust splitter was designed and tested to determine if exhaust particulate could be collected at 32°C (90°F) under high speed cruise conditions (96 to 113 km/hr). If only 25% of the raw exhaust from a 350 CID, V-8 vehicle operating at 113 km/hr for example, this volume of exhaust would be approximately equivalent to the average output of the same vehicle under FTP conditions. In order to accurately measure the exhaust particulate emission rates, the ratio of the exhaust volume introduced into the tunnel to that rejected must be constant and accurately known.

The basic approach was to split the exhaust so that the ratio of the volume flow rates of rejected or vented exhaust to that of exhaust introduced into the tunnel would be 3 to 1 at all times on high speed cruise. Figure C-1 shows a schematic of the exhaust splitter system.

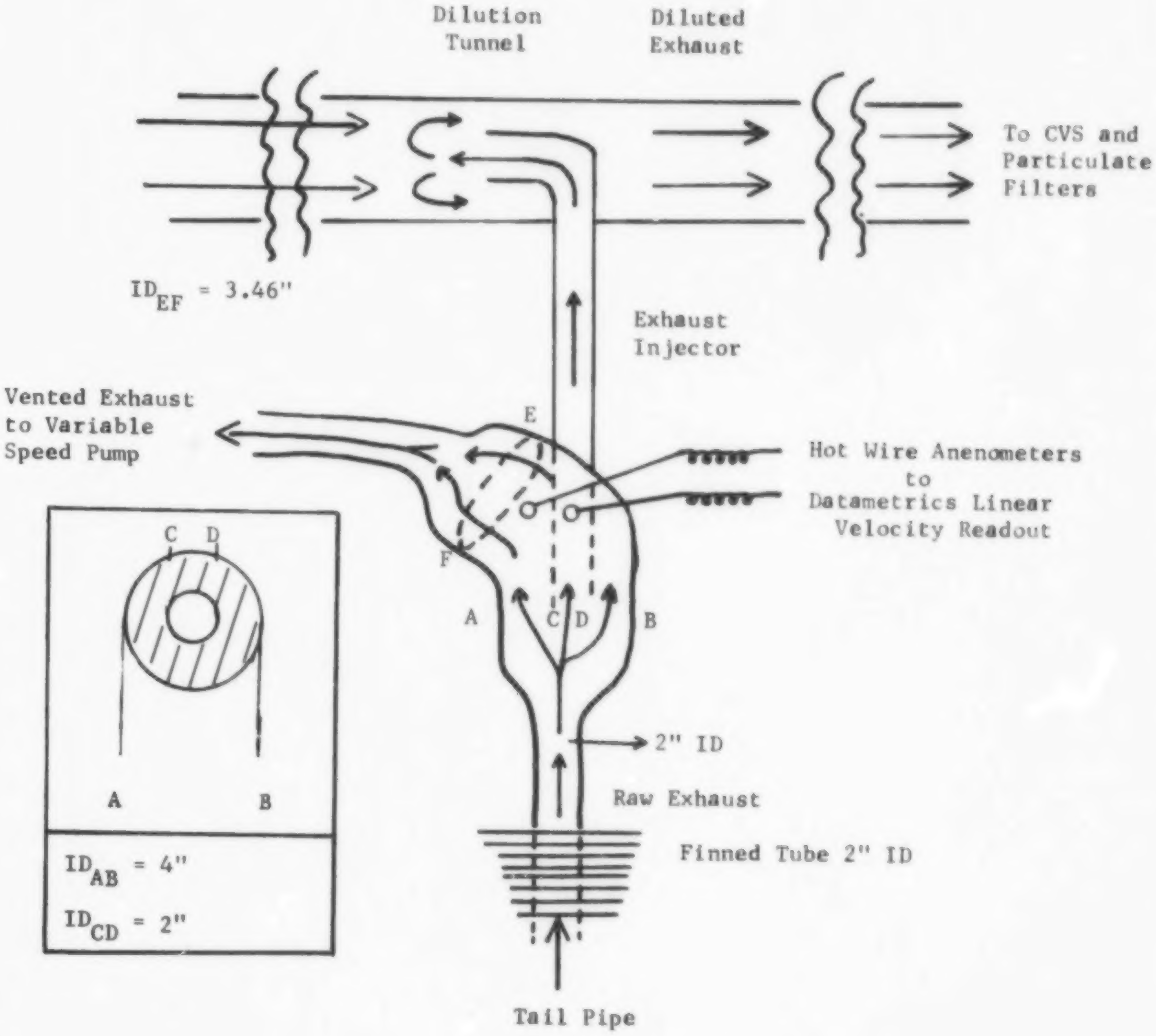
The raw exhaust as it emerges from the finned tube enters concentric pipes designed so that the peripheral laminar area (shaded cross section in the schematic) is three times the area of the smaller central pipe. That is the ID of the smaller central pipe designated as (CD) in the schematic is 2 inches. The ID of the larger pipe, designated as AB in the schematic is 4 inches.

To accommodate the hot wire anenometer probes, the larger pipe turns away from the smaller concentric one and its diameter is reduced to $2\sqrt{3}$ inches, so that the area ratio of the pipes no longer concentrically situated is still 3 to 1. Hot wire anenometers are placed in the middle of the large pipe at the point where the diameter is $2\sqrt{3}$ inches, and into the middle of the two-inch pipe. The two probes, although in separate pipes, are as close to each other as is physically possible so that both would be operating in split raw exhaust streams having the same temperature. Under these conditions, if the linear velocities of the sample streams in each pipe are equal, the volume flow rate ratio in the pipes is 3 to 1.

Initial work using lab air rather than raw exhaust showed that this concept was valid. Laboratory air was pulled into the dilution tunnel by the CVS at total flows of 150 and 225CFM. The lab air entered the tunnel via the diluent air treatment system (dehumidifier, filter and chiller) and the injection leg of the exhaust splitter. No attempts were made to dehumidify the air. Direct reading flowmeters capable of handling large flows were inserted in each leg downstream to the anenometers. The anenometers used were connected to a Datametrics Model 700-6 Anenometer circuit(13).

FIGURE C-1

SCHEMATIC OF EXHAUST SPLITTER



The experimental test was carried out oppositely to how the splitter would be used in practice. For a given total volume flow rate, the flow in the vent leg was adjusted with a variable speed pumps until the volumetric flow rate ratio was 3 to 1. The linear velocities in each leg were indicated on the Datametrics Readout. Table C-1 below shows that the linear velocity results agreed to within about 4%.

TABLE C-1
Performance of Exhaust
Splitter on Lab Air

	Measured Flow Rate (CFM)		Corresponding Linear Velocities (ft/min)			
			Datametrics Readout (Arbitrary Units)		Actual ft/min	
CVS Setting (CFM)	Vent Leg	Inlet Leg	Vent	Inlet	Vent	Inlet
150	72.7	24.5	0.89	0.95	1111	1125
225	132.7	44.0	1.52	1.65	2029	2018

The procedure in an actual run would be to adjust the variable speed pump until the linear velocities in the vent and inlet legs were equal. No volumetric flow rate measurement would be made because it is doubtful that any flow meter would function properly after exposure to hot corrosive exhaust, and any flowmeter in the inlet leg could alter the quantity of particulate matter entering the dilution tunnel. Table C-1 shows that it should not be necessary to measure the volumetric flow rates. All that would be necessary would be to maintain equal linear velocities in leg.

Although Table C-1 shows that this approach is promising, this method has not been successful in actual runs with catalyst equipped vehicles. Several anemometer probes have failed when exposed to hot raw exhaust from oxidation catalyst equipped vehicles. It is probable that corrosion of the sensing wires due to exposure to hot sulfuric acid aerosol is the cause. In several vehicle tests, the sensing wires were missing after the run, or else was attached to only one binding post.

Another approach along the same basic idea was to measure the linear velocities using Pitot tubes, and equalizing the velocities by adjusting the pressure drop in the vent leg using a variable speed pump. The pressure drops were small and subject to rapid oscillations, making equalization extremely difficult. Attempts to damp these oscillations were not successful.

APPENDIX D

BASIS OF SELECTION OF THE SULFUR AND NITROGEN CONTAINING ORGANIC COMPOUNDS WHICH MIGHT APPEAR IN AN AUTO EXHAUST

The rationale for selecting classes of nitrogenous and non-sulfate sulfur compounds as possible exhaust components is based on known chemical reactions which produce these compounds. Only those components known to exist in vehicular exhaust, which can function as precursors to compound types or as reactants involved in their production, are considered. Several examples will be considered in some detail.

Schuchmann and Laidler (14) have shown the existence of alkyl nitriles in automobile exhaust, which are the products of reaction between nitric oxide and alkyl radicals, i.e.,

$$RCH_2\cdot + NO \longrightarrow RCN + H_2O$$

Based on the above reaction, alkyl nitrites could also be a logical exhaust product as a result of reaction between nitric oxide and alkaxy radical as shown below:

$$RO\cdot + NO \longrightarrow RONO$$

Scizinger and Dimitriades (15), have shown that nitroalkanes are components of automobile exhaust. Nitroalkanes could conceivably be made by reaction of alkyl radicals and NO_2. However, it is not necessary to invoke this reaction to account for nitroalkanes. Levy (16), has shown that in the presence of nitric oxide, alkyl nitriles are convented to nitroalkanes.

Ter Hoar, et. al.(17), have reported the presence of nitrates in exhaust particulates. Organic nitrates could be formed by reaction of alkyl nitrites with peroxides as shown below(18):

$$RCH_2ONO + R'OOH \longrightarrow R'OH + RCH_2ONO_2$$

The absence of peroxides in end gas condensate as demonstrated by Alperstein and Bradow(19) and the presence of alcohols(15) and nitrates(17) in automobile exhaust may be the result of the above type of reaction. Although the formation of the aromatic analogues of the nitrogenous compounds listed is less likely than their aliphatic counterparts, tests for the nitrogenous aromatic compounds were also carried out.

Arguments applied to the possible formation of nitrogenous exhaust matter are applicable to the non-sulfate sulfur compounds. For example, sulfinic acids could be produced by reaction of SO_2 and an aromatic species as shown below(2):

$$R\phi{-}H \quad + \quad SO_2 \longrightarrow R\phi{-}SO_2H$$

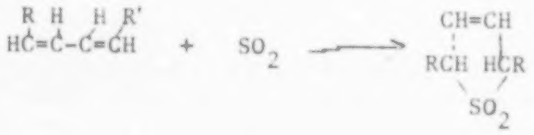
Aromatic sulfonic acids could result from reaction of SO_3 and an aromatic species as shown below(21):

$$R\phi{-}H \quad + \quad SO_3 \longrightarrow R\phi{-}SO_3H$$

There are several factors operating against the formation of aromatic sulfonic acids in auto exhaust: The low concentration of SO_3 in conventional vehicle exhaust, and the greatly reduced level of aromatic species (organics in general) in the exhaust of an oxidation catalyst equipped vehicle. However, if one grants the possibility of aromatic sulfonic acids, the presence of sulfones is also possible by virtue of the following reaction(22):

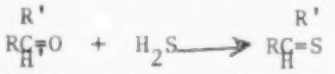
$$R\phi{-}SO_3H \quad + \quad R'\phi{-}H \longrightarrow R\phi{-}SO_2{-}\phi{-}R' \quad + \quad H_2O$$

Another possible mechanism by which sulfones may be formed is by the reaction of SO_2 with a conjugated di-olefin as shown below(23):



$$\overset{R}{HC}{=}\overset{H}{C}{-}\overset{H}{C}{=}\overset{R'}{CH} \quad + \quad SO_2 \longrightarrow \begin{array}{c} CH{=}CH \\ RCH \quad HCR \\ SO_2 \end{array}$$

Sulfur compounds such as thiocarbonyls, sulfides, and mercaptans are possible only under reducing conditions. Should operating conditions, over an oxidation catalyst become net rich, a number of SO_2 reduction products including H_2S are then possible. This condition is unlikely unless engine or system malfunctions occur. Should these malfunctions occur, H_2S could react with various reactive exhaust components such as ketones, aldehydes, and olefins to produce thiocarbonyls and mercaptans as shown below: (14)



$$R\overset{R'}{\underset{H}{C}}{=}O \quad + \quad H_2S \longrightarrow R\overset{R'}{\underset{H}{C}}{=}S \qquad \text{and possible polymers}$$

$$RC{=}O \quad + \quad H_2S \longrightarrow RC{=}S$$

$$(CH_3)_2C{=}CH_2 \quad + \quad H_2S \longrightarrow (CH_3)_3CSH$$

Mercaptans could also possibly be formed by the reaction between alcohols present in exhaust and H_2S as shown below(25):

$ROH + H_2S \longrightarrow RSH$ and H_2O, although this is a less likely route to mercaptans.

In situations where H_2S is produced alkyl isothiocyanates may be produced if notroalkanes are also present by virtue of the following possible pathway (26,27).

$$RCH_2NO_2 \longrightarrow RC\text{-}NHOH$$

$$R\overset{O}{\overset{\|}{C}}\text{-}NHOH \longrightarrow RNCO + H_2O$$

$$RNCO + H_2S \longrightarrow RNCS + H_2O$$

The occurrence of many of the organic sulfur compounds, particularly the thiocarbonyls, sulfides, and mercaptans, in auto exhaust however, is extremely unlikely for the following reasons. The operating conditions favoring H_2S formation (high catalyst temperature and oxygen deficiency) do not normally occur in oxidation catalyst emission control systems, so that H_2S formation over the catalyst is unlikely unless engine or system malfunctions occur(28). Even if H_2S were produced, the formation of a mercaptan by reaction of H_2S with an alcohol becomes more unfavorable with increasing temperature, precisely the conditions assuming oxygen deficiency favorable for H_2S formation. Thermodynamic calculations based on Free Energy of Formation data obtained from Stull, et. al(29) show that in the temperature range of 800 to 1200 F, mercaptans should not form.

The occurrence of nitrogenous and sulfur compounds in automobiles would expected to be at most at trace levels. That they should be present in automotive exhaust particulate is even more remote. For example, if all of the nitrogenous additive was convented to all or any of the nitrogenous compounds discussed, it can readily be shown that there is not sufficient nitrogen containing additive to produce enough of these compounds to co-exist as two phases (vapor plus liquid) at the particulate collection temperature. Only the liquid form could be trapped as particulate, and it cannot exist as a liquid under the test conditions.

Assume that an alkyl nitrile such as valeronitrile $(CH_3)_2$ -CH-$(CH_2)_2CN$ was an exhaust component. At the particulate collection temperature 90F, the vapor pressure of this compound is 12mmHg. At a tunnel flow rate of 450CFM (12,600 liters/min), the minimum production rate of valeronitrile required to maintain the equilibrium vapor pressure calculated from the ideal gas law is:

$$\frac{\text{moles}}{\text{min}} = \frac{(12/760)\ \text{atm}\ (12600)\ \text{lit/min}}{(365^\circ K)\ 82\text{x}10^{-3}\ \text{litatm mole}^{-1}\ \text{deg}^{-1}}$$

$$= 6.65 \text{ moles/min}$$

$$= 645 \text{ gms/min}$$

This production rate is many orders of magnitude greater than that of a nitrogenous exhaust product derived from a nitrogenous additive could possibly be. This applies to all the nitrogenous compounds tested for. Therefore, if nitrogenous additives result in nitrogenous organic compounds as exhaust components, they must exist as gaseous components if they exist at all. The only ways nitrogenous particulate exhaust compounds could exist would be if they were strongly chemadsorbed on particulate matter, or if they survived as high molecular weight nitrogenous components. It is unlikely therefore, that there is an effect of nitrogenous additives on exhaust particulate emissions.

Using a similar argument, it can be shown that it is highly unlikely that non-sulfate sulfur compounds would show up as exhaust particulate. The negative tests obtained for the nitrogenous and non-sulfate sulfur compounds in exhaust particulate substantiates the above discussion.

Coupling this discussion with the negative test results, it may be concluded that there is no exhaust particulate derived from the ashless nitrogenous additives used. It may also be concluded that regarding sulfur containing particulate, sulfate is the overwhelmingly predominant species and most likely only one capable of existing as particulate.

Although the previous discussion pertained to nitrogenous and non-sulfate sulfur containing particulate matter, similar conclusions can be drawn regarding the presence of many of these compounds as gaseous components of exhaust. This would particularly apply to the non-sulfate sulfur compounds, especially the divalent sulfur compounds. For example, consider the formation of COS produced by the following reaction:

$$CO_2 + H_2S \longrightarrow COS + H_2O$$

In raw, undiluted automotive exhaust, the CO_2 and H_2O partial pressure are comparable, greatly exceeding any H_2S present. Consequently, the equilibrium constant for COS formation is the ratio of

$$K = \frac{P_{cos}\ P_{H_2O}}{P_{H_2S}\ P_{CO_2}} = \frac{P_{cos}}{P_{H_2S}}$$

The value of K at temperatures ranging from 800°F to 1160°F ranges from 2.1×10^{-6} to 1.1×10^{-7}. Thus, the COS concentration can only be a negligible fraction of the H_2S concentration. Since H_2S formation is unlikely, and at most would exist at low levels for small time intervals, COS could not be a component of automotive exhaust. Similar types of arguments could be extended to other organic compounds containing di-valent sulfur.

APPENDIX E

RAW DATA

E.1 List of Raw Data Tables

Table	Title
E-1	Gaseous Emissions - Unequipped Mileage Accumulation Vehicle
E-2	- Unequipped Test Vehicle
E-3	- Engelhard Monolithic Oxidation Catalyst
E-4	- Engelhard Pelletized Oxidation Catalyst
E-5	- UOP (1) Monolithic Oxidation Catalyst
E-6	- Matthey-Bishop Monolithic Oxidation Catalyst
E-7	- Grace NO_x Reduction Catalyst
E-8	- Gould NO_x Reduction Catalyst
E-9	- Grace Pelleted Oxidation Catalyst
E-10	- UOP (2) Monolithic Oxidation Catalyst
E-11	- Air Products Pelletized Oxidation Catalyst
E-12	- Sulfate Storage Experiment
E-13	- Engelhard Monolithic Oxidation Catalyst After Misfire
E-14	Metal Derived Particulate Emissions - Unequipped Mileage Accumulation Vehicle Runs (1-15) and Unequipped Test Vehicle Runs (16-30)
E-15	- Engelhard Monolithic Oxidation Catalyst
E-16	- Engelhard Pelletized Oxidation Catalyst
E-17	- UOP (1) Monolithic Oxidation Catalyst
E-18	- Matthey-Bishop Monolithic Oxidation Catalyst
E-19	- Grace Reduction Catalyst
E-20	- Gould NO_x Reduction Catalyst
E-21	- Grace Pelletized Oxidation Catalyst
E-22	- UOP (2) Monolithic Oxidation Catalyst
E-23	- Air Products Pelletized Oxidation Catalyst
E-24	- Sulfate Storage Experiment
E-25	Sulfate Emissions - Unequipped Mileage Accumulation Vehicle
E-26	- Unequipped Test Vehicle
E-27	- Engelhard Monolithic Oxidation Catalyst
E-28	- Engelhard Pelletized Oxidation Catalyst
E-29	- UOP (1) Monolithic Oxidation Catalyst
E-30	- Matthey-Bishop Monolithic Oxidation Catalyst
E-31	- Grace NO_x Reduction Catalyst
E-32	- Gould NO_x Reduction Catalyst
E-33	- Grace Pelletized Oxidation Catalyst
E-34	- UOP (2) Monolithic Oxidation Catalyst
E-35	- Air Products Pelletized Oxidation Catalyst
E-36	- Sulfur Storage Experiment

TABLE E-1

GASEOUS EMISSIONS
UNEQUIPPED MILEAGE ACCUMULATION VEHICLE

Test No.	% Fuel Sulfur	Run Type	Gaseous Emissions, gms/km			
			CO	HC	NO_x	SO_2
1	0.019	75 FTP	8.76	1.23	0.86	---
2	"	Idle (1)	[170.38]	[9.24]	[19.12]	---
3	"	40 (1)	7.54	0.417	0.61	---
4	"	70 (2)	5.90	0.05	1.76	---
5	"	75 FTP	8.58	1.57	0.97	---
6	0.110	75 FTP	9.09	1.38	1.02	0.239
7	"	Idle (1)	[---]	[---]	[---]	---
8	"	40 (1)	---	---	---	---
9	"	70 (2)	2.63	0.06	0.73	0.181
10	"	75 FTP	8.59	1.21	1.00	0.301
11	0.091	75 FTP	9.49	1.62	1.38	0.363
12	"	Idle (1)	[169.92]	[24.43]	[2.93]	[4.47]
13	"	40 (1)	4.23	2.60	0.34	0.154
14	"	70 (2)	2.62	0.010	0.60	0.154
15	"	75 FTP	8.24	1.80	1.17	0.347

0.019% S = EPA furnished reference fuel

0.110% S = EPA reference fuel plus additive package

0.090% = High aromatic fuel plus additive package

75 FTP = 1975 Federal test procedure

Idle (1) = One hour idle

40 (1) = 40 mph (64 km/hr) cruise for one hour

70 (2) = 70 mph (112 km/hr) cruise for two hours

(Idle gaseous emissions, brackets, are in gms/hr)*

TABLE E-2

GASEOUS EMISSIONS
UNEQUIPPED TEST VEHICLE

Test No.	% Fuel Sulfur	Run Type	Gaseous Emissions, gms/km			
			CO	HC	NO_x	SO_2
16	0.019	75 FTP	6.33	0.78	0.97	0.048
17	"	Idle (1)	[21.69]	[10.85]	[3.05]	[1.260]
18	"	40 (1)	3.15	0.18	0.28	[0.025]
19	"	70 (2)	2.32	0.04	0.86	[0.035]
20	"	75 FTP	6.84	3.70	0.78	0.076
21	0.110	75 FTP	6.23	0.71	0.77	0.284
22	"	Idle (1)	[29.4]	[7.06]	[2.20]	[3.262]
23	"	40 (1)	3.09	0.17	0.29	0.202
24	"	70 (2)	1.72	0.05	0.86	0.167
25	"	75 FTP	6.28	0.99	0.85	0.295
26	0.091	75 FTP	7.13	0.75	0.84	0.318
27	"	Idle (1)	[35.14]	[8.56]	[6.30]	[5.26]
28	"	40 (1)	1.92	0.17	0.43	0.160
29	"	70 (2)	00.61	0.05	0.54	0.136
30	"	75 FTP	6.61	0.74	0.84	0.301

0.019% S = EPA furnished reference fuel
0.110% S = EPA reference fuel plus additive package
0.090% = High aromatic fuel plus additive package

75 FTP = 1975 Federal test procedure
Idle (1) = One hour idle
40 (1) = 40 mph (64 km/hr) cruise for one hour
70 (2) = 70 mph (112 km/hr) cruise for two hours
(Idle gaseous emissions, brackets, are in gms/hr)*

TABLE E-3

GASEOUS EMISSIONS
ENGELHARD MONOLITHIC OXIDATION
CATALYST EQUIPPED VEHICLE

Test No.	% Fuel Sulfur	Run Type	Gaseous Emissions, gms/km			
			CO	HC	NO_x	SO_2
36	0.019	75 FTP	3.26	0.29	0.91	∿0
37	"	Idle (1)	[7.70]	[4.45]	[8.66]	0
38	"	40 (1)	0.05	0.04	0.15	0
39	"	70 (2)	---	---	---	0
40	"	75 FTP	1.18	0.63	0.74	0
41	0.110	75 FTP	1.45	0.80	1.20	0.134
42	"	Idle (1)	[5.32]	[5.62]	[3.91]	[2.55]
43	"	40 (1)	0.20	0.08	0.52	0.057
44	"	70 (2)	0.024	0.003	0.19	0.009
45	"	75 FTP	2.03	0.42	0.88	0.139
46	0.091	75 FTP	1.40	0.28	1.33	0.080
47	"	Idle (1)	[7.26]	[6.10]	[3.91]	[2.14]
48	"	40 (1)	0.28	0.08	1.04	0.050
49	"	70 (2)	---	---	---	---
50	"	75 FTP	2.01	0.28	1.31	0.098

0.019% S = EPA furnished reference fuel

0.110% S = EPA reference fuel plus additive package

0.090% = High aromatic fuel plus additive package

75 FTP = 1975 Federal test procedure

Idle (1) = One hour idle

40 (1) = 40 mph (64 km/hr) cruise for one hour

70 (2) = 70 mph (112 km/hr) cruise for two hours

(Idle gaseous emissions, brackets, are in gms/hr)*

TABLE E-4

GASEOUS EMISSIONS
ENGELHARD PELLETIZED OXIDATION
CATALYST EQUIPPED VEHICLE

Test No.	% Fuel Sulfur	Run Type	Gaseous Emissions, gms/km			
			CO	HC	NO_x	SO_2
51	0.019	75 FTP	2.528	0.217	1.370	0.015
52	"	Idle (1)	[0.81]	[1.458]	[0.54]	[0.0]
53	"	40 (1)	0.019	0.016	0.008	0.0
54	"	70 (2)	---	---	---	---
55	"	75 FTP	2.501	0.224	1.318	0.093
56	0.110	75 FTP	1.528	0.349	1.229	0.043
57	"	Idle (1)	[7.506]	[3.964]	[8.73]	[0.544]
58	"	40 (1)	0.154	0.075	0.601	0.0
59	"	70 (2)	0.086	0.029	1.581	0.0
60	"	75 FTP	1.327	0.176	1.013	0.058
61	0.091	75 FTP	2.162	0.324	1.194	0.061
62	"	Idle (1)	[4.676]	[2.333]	[8.932]	0.0
63	"	40 (1)	0.218	0.089	0.740	0.022
64	"	70 (2)	0.044	0.008	3.111	0.129
65	"	75 FTP	2.808	0.219	1.171	0.066

0.019% S = EPA furnished reference fuel

0.110% S = EPA reference fuel plus additive package

0.090% = High aromatic fuel plus additive package

75 FTP = 1975 Federal test procedure

Idle (1) = One hour idle

40 (1) = 40 mph (64 km/hr) cruise for one hour

70 (2) = 70 mph (112 km/hr) cruise for two hours

(Idle gaseous emissions, brackets, are in gms/hr)*

TABLE E-5

GASEOUS EMISSIONS
UOP(1) MONOLITHIC OXIDATION CATALYST
EQUIPPED TEST VEHICLE

Test No.	% Fuel Sulfur	Run Type	Gaseous Emissions, gms/km			
			CO	HC	NO_x	SO_2
66	0.019	75 FTP	2.652	0.274	1.091	0.061
67	"	Idle (1)	[22.766]	[11.416]	[6.728]	[0.0]
68	"	40 (1)	0.129	0.042	0.694	0.0
69	"	70 (2)	0.174	0.018	1.955	0.031
70	"	75 FTP	1.770	0.191	0.927	0.029
71	0.110	75 FTP	1.742	0.250	1.079	0.190
72	"	Idle (1)	[4.946]	[4.277]	[5.098]	[0.0]
73	"	40 (1)	0.119	0.048	0.505	0.031
74	"	70 (2)	0.121	0.014	0.118	0.117
75	"	75 FTP	2.124	0.264	0.622	0.186
76	0.091	75 FTP	1.800	0.191	1.277	0.074
77	"	Idle (1)	[4.136]	[4.158]	[6.836]	[0.0]
78	"	40 (1)	0.132	0.033	0.706	0.043
79	"	70 (2)	0.147	0.013	3.570	0.107
80	"	75 FTP	1.863	0.150	1.305	0.004

0.019% S = EPA furnished reference fuel
0.110% S = EPA reference fuel plus additive package
0.090% = High aromatic fuel plus additive package

75 FTP = 1975 Federal test procedure
Idle (1) = One hour idle
40 (1) = 40 mph (64 km/hr) cruise for one hour
70 (2) = 70 mph (112 km/hr) cruise for two hours
(Idle gaseous emissions, brackets, are in gms/hr)*

TABLE E-6

GASEOUS EMISSIONS
MATTHEY BISHOP MONOLITHIC OXIDATION CATALYST EQUIPPED TEST VEHICLE

Test No.	% Fuel Sulfur	Run Type	Gaseous Emissions, gms/km CO	HC	NO_x	SO_2*
81	0.019	75 FTP	1.373	0.232	1.083	0.031
82	"	Idle (1)	[8.834]	[5.584]	[11.524]	[0.961]
83	"	40 (1)	0.200	0.047	0.598	0.037
84	"	60 (2)**	0.427	0.033	2.208	0.022
85	"	75 FTP	0.959	0.146	0.578	0.023
86	0.110	75 FTP	1.035	0.241	1.116	0.245
87	"	Idle (1)	[8.067]	[6.361]	[7.020]	[3.694]
88	"	40 (1)	0.267	0.058	0.648	0.197
89	"	60 (2)	0.555	0.033	2.430	0.213
90	"	75 FTP	2.663	0.323	1.136	0.275
91	0.091	75 FTP	1.040	0.244	1.313	0.233
92	"	Idle (1)	[5.430]	[4.061]	[8.381]	[2.960]
93	"	40 (1)	0.288	0.049	30.890	0.160
94	"	60 (2)	0.549	0.030	2.938	0.194
95	"	75 FTP	2.087	0.253	2.112	0.388

0.019% S = EPA furnished reference fuel

0.110% S = EPA reference fuel plus additive package

0.090% = High aromatic fuel plus additive package

75 FTP = 1975 Federal test procedure

Idle (1) = One hour idle

40 (1) = 40 mph (64 km/hr) cruise for one hour

60 (2) = 60 mph (96 km/hr) cruise for two hours

(Idle gaseous emissions, brackets, are in gms/hr)*

* SO_2 calibrated from SO_2 in air calibration curve (no correction factor was used)

** 60 mph (96.54 km/hr) supplants the former 70 mph cruise test runs

TABLE E-7

GASEOUS EMISSIONS
GRACE NO_x REDUCTION
CATALYST EQUIPPED VEHICLE

Test No.	% Fuel Sulfur	Run Type	Gaseous Emissions, gms/km			
			CO	HC	NO_x	SO_2
96	0.019	75 FTP	10.177	0.375	2.006	0.142
97	"	Idle (1)	[42.206]	[4.19]	[8.906]	[0.972]
98	"	40 (1)	0.350	0.055	1.469	0.027
99	"	60 (2)	1.913	0.057	3.175	0.040
100	"	75 FTP	7.298	0.498	1.907	0.031
101	0.110	75 FTP	10.657	0.446	2.138	0.339
102	"	Idle (1)	[98.550]	[11.804]	[10.530]	[4.892]
103	"	40 (1)	0.603	0.099	1.976	0.137
104	"	60 (2)	0.208	0.024	1.682	0.084
105	"	75 FTP	10.439	0.455	1.860	0.333
106	0.091	75 FTP	10.828	0.454	2.529	0.321
107	"	Idle (1)	[41.926]	[13.640]	[7.873]	[7.495]
108	"	40 (1)	0.474	0.077	1.842	0.131
109	"	60 (2)	0.350	0.057	4.783	0.202
110	"	75 FTP	14.262	0.531	2.705	0.346

0.019% S = EPA furnished reference fuel
0.110% S = EPA reference fuel plus additive package
0.090% = High aromatic fuel plus additive package

75 FTP = 1975 Federal test procedure
Idle (1) = One hour idle
40 (1) = 40 mph (64 km/hr) cruise for one hour
60 (2) = 60 mph (96 km/hr) cruise for two hours
(Idle gaseous emissions, brackets, are in gms/hr)*
Exhaust gas recycle and air pump disconnected

TABLE E-8

GASEOUS EMISSIONS
GOULD NO_x REDUCTION CATALYST
EQUIPPED VEHICLE

Test No.	% Fuel Sulfur	Run Type	Gaseous Emissions, gms/km			
			CO	HC	NO_x	SO_2
111	0.019	75 FTP	12.560	0.582	1.515	0.119
112	"	Idle (1)	[75.589]	[7.247]	[1.205]	[0.035]
113	"	40 (1)	0.131	0.055	1.721	0.024
114	"	60 (2)	0.006	0.003	0.319	0.004
115	"	75 FTP	8.102	0.285	1.890	0.053
116	0.110	75 FTP	11.558	0.430	2.032	0.290
117	"	Idle (1)	[5.195]	[3.424]	[6.134]	[1.62]
118	"	40 (1)	0.180	0.046	2.083	0.139
119	"	60 (2)	0.014	0.005	0.503	0.020
120	"	75 FTP	6.458	0.297	2.967	0.271
121	0.091	75 FTP	6.173	0.452	1.966	0.243
112	"	Idle (1)	[9.050]	[4.428]	[6.588]	[1.577]
123	"	40 (1)	0.140	0.038	2.249	0.107
124	"	60 (2)	0.066	0.023	3.865	0.125
125	"	75 FTP	6.466	0.327	2.620	0.242

0.019% S = EPA furnished reference fuel
0.110% S = EPA reference fuel plus additive package
0.090% = High aromatic fuel plus additive package

75 FTP = 1975 Federal test procedure
Idle (1) = One hour idle
40 (1) = 40 mph (64 km/hr) cruise for one hour
70 (2) = 70 mph (112 km/hr) cruise for two hours
(Idle gaseous emissions, brackets, are in gms/hr)*
Exhaust gas recycle and air pump disconnected

TABLE E-9

GASEOUS EMISSIONS
GRACE PELLETIZED OXIDATION
CATALYST EQUIPPED VEHICLE

Test No.	% Fuel Sulfur	Run Type	Gaseous Emissions, gms/km			
			CO	HC	NO_x	SO_2
126	0.019	75 FTP	1.563	0.182	1.188	0.032
127	"	Idle (1)	[3.000]	[4.212]	[6.005]	[0.000]
128	"	40 (1)	0.116	0.027	0.686	0.006
129	"	60 (2)	0.051	0.015	1.788	0.022
130	"	75 FTP	1.739	0.150	1.215	0.010
131	0.110	75 FTP	1.519	0.162	1.104	0.070
132	"	Idle (1)	[3.445]	[3.726]	[6.977]	[0.389]
133	"	40 (1)	0.103	0.028	0.016	0.076
134	"	60 (2)	0.048	0.011	1.887	0.131
135	"	75 FTP	0.966	0.164	1.323	0.131
136	0.091	75 FTP	1.274	0.154	1.332	0.072
137	"	Idle (1)	[6.826]	[4.039]	[7.571]	[0.972]
138	"	40 (1)	0.278	0.030	0.813	0.055
139	"	60 (2)	0.063	0.011	2.801	0.005
140	"	75 FTP	2.053	0 134	1.412	0.081

0.019% S = EPA furnished reference fuel

0.110% S = EPA reference fuel plus additive package

0.090% = High aromatic fuel plus additive package

75 FTP = 1975 Federal test procedure

Idle (1) = One hour idle

40 (1) = 40 mph (64 km/hr) cruise for one hour

60 (2) = 60 mph (96 km/hr) cruise for two hours

(Idle gaseous emissions, brackets, are in gms/hr)*

TABLE E-10

GASEOUS EMISSIONS UOP(2) MONOLITHIC OXIDATION CATALYST EQUIPPED VEHICLE

Test No.	% Fuel Sulfur	Run Type	Gaseous Emissions, gms/km			
			CO	HC	NO_x	SO_2
141	0.019	75 FTP	0.666	0.101	1.231	0.008
142	"	Idle (1)	[2.862]	[3.845]	[8.597]	[0.000]
143	"	40 (1)	0.105	0.016	0.776	0.000
144	"	60 (2)	0.089	0.018	2.877	0.018
145	"	75 FTP	1.431	0.127	1.150	0.028
146	0.110	75 FTP	0.768	0.098	1.303	0.046
147	"	Idle (1)	[4.471]	[4.439]	[8.921]	[0.194]
148	"	40 (1)	0.098	0.025	0.770	0.045
149	"	60 (2)	0.070	0.021	1.946	0.110
150	"	75 FTP	0.653	0.105	1.316	0.146
151	0.091	75 FTP	0.805	0.154	1.270	0.094
152	"	Idle (1)	[4.018]	[4.374]	[5.918]	[0.389]
153	"	40 (1)	0.103	0.023	0.829	0.061
154	"	60 (2)	0.065	0.012	2.574	0.005
155	"	75 FTP	1.227	0.239	1.345	0.187

0.019% S = EPA furnished reference fuel

0.110% S = EPA reference fuel plus additive package

0.090% = High aromatic fuel plus additive package

75 FTP = 1975 Federal test procedure

Idle (1) = One hour idle

40 (1) = 40 mph (64 km/hr) cruise for one hour

70 (2) = 60 mph (96 km/hr) cruise for two hours

(Idle gaseous emissions, brackets, are in gms/hr)*

TABLE E-11

GASEOUS EMISSIONS
AIR PRODUCTS PELLETIZED
OXIDATION CATALYST EQUIPPED VEHICLE

Test No.	% Fuel Sulfur	Run Type	Gaseous Emissions, gms/km			
			CO	HC	NO_x	SO_2
156	0.019	75 FTP	3.825	0.268	1.113	0.028
157	"	Idle (1)	[4.838]	[3.996]	[14.515]	[0.000]
158	"	40 (1)	0.049	0.017	0.945	0.002
159	"	60 (2)	0.027	0.010	1.211	0.016
160	"	75 FTP	1.860	0.115	0.849	0.001
161	0.110	75 FTP	4.607	0.185	0.840	0.040
162	"	Idle (1)	[4.126	[2.754]	[8.64]	[0.000]
163	"	40 (1)	0.109	0.027	0.352	0.030
164	"	60 (2)	0.041	0.015	1.021	0.080
165	"	75 FTP	1.012	0.135	0.854	0.042
166	0.091	75 FTP	1.089	0.170	1.241	0.082
167	"	Idle (1)	[2.786]	[2.970]	[8.402]	[0.184]
168	"	40 (1)	0.160	0.016	0.948	0.044
169	"	60 (2)	0.049	0.013	2.024	0.096
170	"	75 FTP	1.421	0.174	1.172	0.076

0.019% S = EPA furnished reference fuel

0.110% S = EPA reference fuel plus additive package

0.090% = High aromatic fuel plus additive package

75 FTP = 1975 Federal test procedure

Idle (1) = One hour idle

40 (1) = 40 mph (64 km/hr) cruise for one hour

60 (2) = 60 mph (96 km/hr) cruise for two hours

(Idle gaseous emissions, brackets, are in gms/hr)*

TABLE E-12

GASEOUS EMISSIONS, TEST VEHICLE EQUIPPED WITH ENGELHARD PELLETIZED OXIDATION CATALYST AFTER CATALYST WAS CONDITIONED ON A 0.091% S FUEL FOR 3200 KM ON THE FEDERAL DURABILITY CYCLE

Test No.	% Fuel Sulfur	Run Type	Emission Rates, gms/km CO	HC	NO_x	SO_2
171	0.019	75 FTP	1.225	0.192	1.201	0.050
172	"	Idle (1)	[3.283]	[5.411]	[10.033]	[0.983]
173	"	40 (1)	0.137	0.042	0.627	0.016
174	"	60 (2)	0.040	0.014	2.472	0.088
175	"	75 FTP	1.011	0.193	1.092	0.077

TABLE E-13

GASEOUS EMISSIONS, TEST VEHICLE EQUIPPED WITH ENGELHARD MONOLITHIC OXIDATION CATALYST*

Test No.	% Fuel Sulfur	Run Type	Emission Rates, gms/km CO	HC	NO_x	SO_2
31	0.019	75 FTP	0.77	0.70	1.66	0.035
32	"	Idle (1)	[6.11]	[2.08]	[6.98]	[1.54]
33	"	40 (1)	0.22	0.050	0.38	0.045
34	"	70 (2)	0.15*	0.010	0.18	0.003
35	"	75 FTP	4.84	0.92	1.11	0.057

---

* Temperature runaway due to misfire 19 minutes into the run resulting in catalyst deactivation, compare runs 31 and 35. The emission rates for Test No. 34 are presented on normalized basis.

A second catalyst of this type was conditioned and screened (Table E-3) Runs 36-50.

TABLE E-14

METAL DERIVED EXHAUST PARTICULATE EMISSIONS
BASE CASE RUNS WITH UNEQUIPPED MILEAGE ACCUMULATION VEHICLE RUNS (1-15) AND UNEQUIPPED TEST VEHICLE RUNS (16-30)

Test No.	Run Type	% Fuel Sulfur	EMISSION RATE, GMS/KM AS INDICATED METAL*							
			Ca	Al	Zn	Cr	Fe	Cu	Ni	Pb
1	75 FTP	0.019	0.00025	<0.00005	0.00035	0.00005	0.00134	0.00012	<0.00005	0.00043
2	Idle (1)	"	[<0.0008]	[<0.0008]	[0.0008]	[<0.0008]	[0.00032]	[<0.0008]	[<0.0008]	[0.0008]
3	40 (1)	"	0.00003	<0.00001	0.00010	0.00003	0.00022	0.00002	0.00001	0.00011
4	70 (2)	"	0.00011	6×10^{-6}	0.00009	<0.00001	0.00015	$<6 \times 10^{-6}$	<0.00001	0.00009
5	75 FTP	"	0.00016	0.00006	0.00064	0.00005	0.00080	0.00016	0.00004	0.00042
6	75 FTP	0.110	0.00014	0.00020	0.00027	0.00007	0.00022	0.00014	0.00005	0.00058
7	Idle (1)	"	[0.0022]	[0.0015]	[0.0035]	[0.0009]	0.0080	[0.0019]	[0.0009]	[0.0063]
8	40 (1)	"	0.00004	0.00002	0.00005	0.00002	0.00022	0.00002	0.00001	0.00014
9	70 (2)	"	0.00001	0.00001	0.00003	<0.00001	0.00012	0.00001	<0.00001	0.00006
10	75 FTP	"	0.00017	0.00006	0.00080	0.00009	0.00132	0.00031	0.00008	0.00006
11	75 FTP	0.091	0.00014	0.00006	0.00027	0.00020	0.00134	0.00027	0.00019	0.00087
12	Idle (1)	"	[0.0012]	[<0.0004]	[0.0006]	[0.0006]	[0.0040]	[<0.0004]	[<0.0004]	[0.0122]
13	40 (1)	"	0.00002	$<6 \times 10^{-6}$	0.00002	$<6 \times 10^{-6}$	0.00003	$<6 \times 10^{-6}$	$<6 \times 10^{-6}$	0.00010
14	70 (2)	"	0.00001	<0.00001	0.00003	$<6 \times 10^{-6}$	0.00008	0.00002	0.00001	0.00006
15	75 FTP	"	0.00009	0.00004	0.00040	0.00005	0.00052	0.00025	0.00005	0.00049
16	75 FTP	0.019	0.00007	0.00007	0.00016	0.00007	0.00121	0.00047	0.00008	0.00070
17	Idle (1)	"	[0.0004]	[<0.0004]	[0.0006]	[<0.0004]	[0.0037]	[0.0009]	[<0.0004]	[0.0024]
18	40 (1)	"	0.00001	$<6 \times 10^{-6}$	0.00001	<0.00001	0.00009	$<6 \times 10^{-6}$	$<6 \times 10^{-6}$	0.00005
19	70 (2)	"	$<6 \times 10^{-6}$	$<6 \times 10^{-6}$	0.00001	$<6 \times 10^{-6}$	0.00006	0.00004	$<6 \times 10^{-6}$	0.00004
20	75 FTP	"	0.00002	<0.00002	<0.00002	<0.00002	0.00004	0.00002	<0.00002	<0.00002
21	75 FTP	0.116	0.00005	0.00004	0.00007	0.00012	0.00123	0.00040	0.00009	0.00062
22	Idle (1)	"	[<0.0004]	[<0.0004]	[0.0004]	[<0.0004]	[0.0005]	[0.0008]	[<0.0004]	[0.0069]
23	40 (1)	"	0.00002	$<6 \times 10^{-6}$	0.00001	$<6 \times 10^{-6}$	0.00004	0.00002	$<6 \times 10^{-6}$	0.00021
24	70 (2)	"	$<6 \times 10^{-6}$	$<6 \times 10^{-6}$	<0.00001	$<6 \times 10^{-6}$	0.00004	0.00001	<0.00001	0.00010
25	75 FTP	"	0.00004	<0.00002	0.00006	<0.00002	0.00028	0.00037	<0.00002	0.00042
26	75 FTP	0.091	0.00007	0.00004	0.00010	0.00004	0.00091	0.00021	0.00004	0.00059
27	Idle (1)	"	[0.0004]	[<0.0004]	[<0.0004]	[<0.0004]	[0.0018]	[0.0008]	[<0.0004]	[0.0004]
28	40 (1)	"	0.00001	$<6 \times 10^{-6}$	$<6 \times 10^{-6}$	$<6 \times 10^{-6}$	0.00002	0.00002	$<6 \times 10^{-6}$	0.00011
29	70 (2)	"	<0.00001	$<6 \times 10^{-6}$	<0.00001	$<6 \times 10^{-6}$	0.00006	0.00002	$<6 \times 10^{-6}$	0.00009
30	75 FTP	"	0.00002	<0.00002	0.00007	<0.00002	0.00031	0.00039	<0.00002	0.00037

75 FTP = 1975 Federal Test Procedure
Idle (1) = one hour idle
40 (1) = 40 mph (64 km/hr) cruise for one hour
70 (2) = 70 mph (112 km/hr) cruise for two hours

* Bracketed numbers are idle emission rates of metals in gms/hour.

TABLE E-15

METAL DERIVED EXHAUST PARTICULATE EMISSIONS
TEST VEHICLE EQUIPPED WITH ENGELHARD MONOLITHIC OXIDATION CATALYST

Test No.	Run Type	% Fuel Sulfur	EMISSION RATE, GMS/KM AS INDICATED METAL*							
			Ca	Al	Zn	Cr	Fe	Cu	Ni	Pb
31	75 FTP	0.019	0.00010	>0.00010	>0.00033	0.00013	0.00202	0.00051	0.00010	0.00100
32	Idle (1)	"	[<0.00180]	[0.00180]	[0.00180]	[0.00180]	[0.03600]	[0.00920]	[0.00180]	[0.0180]
33	40 (1)	"	0.00004	<0.00003	<0.00003	<0.00003	0.00010	<0.00003	<0.00003	0.00011
34	70 (2)	"	0.00021	0.00079	0.00204	0.00031	0.00440	0.00115	0.00021	0.00440
35	75 FTP	"	0.00016	0.00051	0.00202	0.00025	0.00202	0.00092	0.00022	0.00101
36 ✦	75 FTP	0.019	0.00010	0.00029	>0.00100	0.00016	>0.00200	0.00038	<0.00010	>0.00100
37	Idle (1)	"	[0.00180]	[0.00400]	[0.01440]	[<0.00180]	[>0.0018]	[<0.00180]	[<0.0018]	[0.00680]
38	40 (1)	"	<0.00003	0.00005	0.00011	<0.00003	0.00021	<0.00003	<0.00003	0.00015
39	70 (2)	"	0.00009	0.00016	0.00027	<0.00058	>0.00058	0.00008	<0.00058	0.00046
40	75 FTP	"	0.00013	<0.00010	0.00039	<0.00010	>0.00100	<0.00010	<0.00010	0.00056
41	75 FTP	0.110	0.00016	0.00021	0.00100	0.00037	>0.00202	0.00075	0.00020	0.00101
42	Idle (1)	"	[0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.00320]	[<0.00180]	[<0.00180]	[0.00320]
43	40 (1)	"	0.00003	0.00004	0.00016	0.00003	>0.00028	0.00005	0.00004	0.00024
44	70 (2)	"	<0.00002	0.00003	0.00015	0.00004	>0.00020	0.00006	0.00004	>0.00020
45	75 FTP	"	<0.00010	<0.00010	0.00048	<0.00010	>0.00100	0.00045	<0.00010	>0.00100
46	75 FTP	0.091	<0.00010	<0.00010	0.00043	0.00019	>0.00100	0.00065	0.00020	0.00100
47	Idle (1)	"	[<0.00180]	[<0.00180]	[0.00220]	[<0.00180]	[0.00240]	[<0.00180]	[<0.00180]	[0.00400]
48	40 (1)	"	<0.00003	<0.00003	0.00003	<0.00003	0.00006	<0.00003	<0.00003	0.00004
49	70 (2)	"	<0.00001	<0.00001	>0.00024	0.00001	>0.00012	0.00003	<0.00001	>0.00012
50	75 FTP	"	<0.00010	<0.00010	0.00079	0.00011	>0.00100	0.00072	0.00015	0.00085

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* Bracketed numbers are idle emission rates of metals in gms/hour.

✦ Replacement PTX-IIB (Runs 36-50) after first PTX-IIB deactivated (Run 34) due to excessive temperature rise resulting from misfire.

TABLE E-16

METAL DERIVED EXHAUST PARTICULATE EMISSIONS
TEST VEHICLE EQUIPPED WITH ENGELHARD PELLETIZED OXIDATION CATALYST

EMISSION RATE, GMS/KM AS INDICATED METAL*

Test No.	Run Type	% Fuel Sulfur	Ca	Al	Zn	Cr	Fe	Cu	Ni	Pb
51	75 FTP	0.019	0.00010	0.00026	0.00076	0.00021	>0.00202	0.00025	0.00019	>0.00100
52	Idle (1)	"	[<0.00180]	[<0.00180]	[0.00260]	[<0.01800]	[>0.01800]	[<0.01800]	[<0.00180]	[0.00860]
53	40 (1)	"	0.00003	<0.00003	0.00004	<0.00003	0.00028	0.00004	0.00003	0.00016
54	70 (2)	"	0.00004	>0.00028	>0.00057	>0.00028	>0.00057	>0.00028	0.00026	>0.00057
55	75 FTP	"	<0.00010	>0.00100	>0.00200	0.00024	>0.00200	0.00059	0.00019	>0.00100
56	75 FTP	0.110	<0.00010	0.00046	0.00037	0.00028	>0.00202	0.00048	0.00026	>0.00202
57	Idle (1)	"	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.00760]	[<0.00180]	[<0.00180]	[0.00400]
58	40 (1)	"	<0.00003	<0.00003	0.00005	<0.00003	0.00018	<0.00003	<0.00003	0.00015
59	70 (2)	"	<0.00004	0.00006	0.00012	0.00005	0.00073	0.00010	0.00006	>0.00036
60	75 FTP	"	<0.00010	0.00016	0.00019	<0.00010	>0.00100	0.00043	<0.00010	0.00050
61	75 FTP	0.091	0.00024	0.00020	0.00027	0.00018	>0.00101	0.00037	0.00021	0.00076
62	Idle (1)	"	[0.00380]	[0.00200]	[<0.00180]	[<0.00180]	[0.00620]	[<0.00180]	[<0.00180]	0.00200
63	40 (1)	"	0.00006	<0.00003	<0.00003	<0.00003	0.00023	<0.00003	<0.00003	0.00007
64	70 (2)	"	0.00002	0.00001	0.00002	<0.00001	>0.00010	0.00001	<0.00001	0.00003
65	75 FTP	"	0.00029	0.00022	0.00075	0.00012	>0.00202	0.00078	0.00015	0.00057

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* Bracketed numbers are idle emission rates in gms/hour.

TABLE E-17

METAL DERIVED EXHAUST PARTICULATE EMISSIONS
TEST VEHICLE EQUIPPED WITH UOP (1) MONOLITHIC OXIDATION CATALYST

EMISSION RATE, GMS/KM AS INDICATED METAL*

Test No.	Run Type	% Fuel Sulfur	Ca	Al	Zn	Cr	Fe	Cu	Ni	Pb
66	75 FTP	0.019	0.00025	0.00030	0.00035	0.00015	>0.00101	0.00030	0.00017	0.00059
67	Idle (1)	"	[0.00240]	[0.00180]	[<0.00180]	[<0.00180]	[0.00740]	[<0.00180]	[<0.00180]	[<0.00180]
68	40 (1)	"	0.00005	<0.00003	<0.00003	<0.00003	0.00010	<0.00003	<0.00003	0.00004
69	70 (2)	"	0.00002	0.00002	0.00008	0.00002	0.00016	0.00003	<0.00001	0.00008
70	75 FTP	"	0.00015	0.00031	0.00100	<0.00010	>0.00202	0.00060	<0.00010	0.00053
71	75 FTP	0.110	0.00018	0.00032	0.00043	0.00026	>0.00202	0.00028	0.00027	0.00087
72	Idle (1)	"	[0.00440]	[0.00640]	[0.00280]	[0.00240]	[>0.01800]	[0.00260]	[0.00260]	[0.00780]
73	40 (1)	"	0.00005	0.00003	0.00004	<0.00003	0.00021	<0.00003	<0.00003	0.00007
74	70 (2)	"	<0.00010	0.00001	0.00001	<0.00001	>0.00008	<0.00001	<0.00001	0.00002
75	75 FTP	"	0.00020	0.00018	0.00022	<0.00010	0.00087	0.00034	<0.00010	0.00029
76	75 FTP	0.091	0.00019	0.00016	0.00025	0.00012	0.00202	0.00030	0.00010	0.00037
77	Idle (1)	"	[0.00380]	[<0.00180]	[<0.00180]	[<0.00180]	[0.00280]	[0.00180]	[<0.00180]	[0.00200]
78	40 (1)	"	0.00006	<0.00003	<0.00003	<0.00003	0.00016	<0.00003	<0.00003	0.00014
79	70 (2)	"	0.00007	0.00007	0.00016	0.00008	0.00016	0.00008	0.00008	>0.00008
80	75 FTP	"	0.00022	0.00021	0.00018	<0.00010	0.00085	0.00038	<0.00010	0.00039

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* Bracketed numbers are idle emission rates in gms/hour.

TABLE E-18

METAL DERIVED EXHAUST PARTICULATE EMISSIONS
TEST VEHICLE EQUIPPED WITH MATTHEY-BISHOP MONOLITHIC OXIDATION CATALYST

Test No.	Run Type	% Fuel Sulfur	EMISSION RATE, GMS/KM AS INDICATED METAL*							
			Ca	Al	Zn	Cr	Fe	Cu	Ni	Pb
81	75 FTP	0.019	<0.00010	0.00012	0.00024	<0.00010	>0.00101	<0.00010	<0.00010	0.00514
82	Idle (1)	"	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.01820]	[<0.00180]	[<0.00180]	[0.00300]
83	40 (1)	"	<0.00003	<0.00003	<0.00003	<0.00003	0.00017	<0.00003	<0.00003	0.00014
84	60 (2)	"	<0.00001	0.00002	>0.00010	0.00001	>0.00020	0.00004	<0.00001	>0.00010
85‡	75 FTP	"	--	--	--	--	--	--	--	--
86‡	75 FTP	0.110	--	--	--	--	--	--	--	--
87	Idle (1)	"	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.00360]	[<0.00180]	[<0.00180]	[0.00280]
88	40 (1)	"	0.00003	<0.00003	0.00003	<0.00003	>0.00030	<0.00003	<0.00003	0.00013
89	60 (2)	"	<0.00001	<0.00001	0.00008	0.00001	>0.00018	0.00002	<0.00001	0.00009
90	75 FTP	"	<0.00010	<0.00010	0.00018	<0.00010	0.00095	0.00030	<0.00010	0.00034
91	75 FTP	0.091	<0.00010	<0.00010	0.00013	<0.00010	>0.00020	0.00039	<0.00010	0.00048
92	Idle (1)	"	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.00600]	[<0.00180]	[<0.00180]	[0.00240]
93	40 (1)	"	<0.00003	<0.00003	0.00007	<0.00003	0.00025	<0.00003	<0.00003	0.00004
94	60 (2)	"	0.00001	0.00001	>0.00010	<0.00001	>0.00020	0.00003	<0.00001	>0.00010
95	75 FTP	"	<0.00010	<0.00010	0.00020	<0.00010	>0.00101	0.00037	0.00010	0.00029

* Bracketed numbers are idle emission rates in gms/hour

‡ Samples 85, 86 Submitted to EPA for Platinum Analysis

TABLE E-19

METAL DERIVED EXHAUST PARTICULATE EMISSIONS
TEST VEHICLE EQUIPPED WITH GRACE REDUCTION CATALYST

EMISSION RATE, GMS/KM AS INDICATED METAL*

Test No.	Run Type	% Fuel Sulfur	Ca	Al	Zn	Cr	Fe	Cu	Ni	Pb
96	75 FTP	0.019	<0.00010	<0.00010	0.00025	<0.00010	0.00064	0.00016	<0.00010	0.00016
97	Idle (1)	"	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.00580]	[<0.00180]	[<0.00180]	[0.00200]
98	40 (1)	"	<0.00003	<0.00003	<0.00003	<0.00003	0.00014	<0.00003	<0.00003	0.00005
99	60 (2)	"	<0.00001	<0.00001	0.00008	<0.00001	>0.00009	<0.00001	<0.00001	0.00005
100	75 FTP	"	<0.00010	<0.00010	0.00045	<0.00010	>0.00200	0.00025	<0.00010	0.00046
101	75 FTP	0.110	<0.00010	0.00010	0.00021	<0.00010	>0.00100	0.00017	<0.00010	0.00045
102	Idle (1)	"	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.00240]
103	40 (1)	"	<0.00006	<0.00006	<0.00006	<0.00006	>0.00056	<0.00006	<0.00006	0.00010
104	60 (2)	"	<0.00001	<0.00001	>0.00010	<0.00001	>0.00009	0.00002	<0.00001	0.00006
105	75 FTP	"	<0.00010	<0.00010	0.00016	<0.00010	0.00028	0.00021	<0.00010	0.00019
106	75 FTP	0.091	<0.00010	<0.00010	<0.00010	<0.00010	0.00020	0.00016	<0.00010	0.00025
107	Idle (1)	"	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.00220]	[<0.00180]	[<0.00180]	[0.00300]
108	40 (1)	"	<0.00003	<0.00003	<0.00003	<0.00003	0.00011	<0.00003	<0.00003	0.00007
109	60 (2)	"	<0.00001	<0.00001	0.00005	<0.00001	0.00005	0.00001	<0.00001	0.00009
110	75 FTP	"	<0.00010	<0.00010	0.00027	<0.00010	0.00062	0.00037	<0.00010	0.00036

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* Bracketed numbers are idle emission rates of metals in gms/hour.

TABLE E-20

METAL DERIVED EXHAUST PARTICULATE EMISSIONS
TEST VEHICLE EQUIPPED WITH GOULD NO_x REDUCTION CATALYST

EMISSION RATE, GMS/KM AS INDICATED METAL*

Test No.	Run Type	% Fuel Sulfur	Ca	Al	Zn	Cr	Fe	Cu	Ni	Pb
111	75 FTP	0.019	<0.00010	0.00016	0.00012	<0.00010	>0.00100	0.00030	>0.00202	0.00036
112	Idle (1)	"	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.00400]	[<0.00180]	[0.01040]	[0.00200]
113	40 (1)	"	<0.00003	<0.00003	<0.00003	<0.00003	0.00006	<0.00003	0.00016	0.00003
114	60 (2)	"	<0.00001	<0.00001	<0.00001	<0.00001	0.00004	<0.00001	0.00008	0.00006
115	75 FTP	"	<0.00010	<0.00010	<0.00010	<0.00010	<0.00010	0.00017	>0.00106	0.00017
116	75 FTP	0.110	<0.00010	<0.00010	0.00016	<0.00010	0.00058	0.00010	0.00047	0.00026
117	Idle (1)	"	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.00260]	[<0.00180]
118	40 (1)	"	<0.00003	<0.00003	<0.00003	<0.00003	0.00008	<0.00003	0.00005	0.00002
119	60 (2)	"	<0.00001	0.00002	0.00006	<0.00001	>0.00020	0.00003	0.00010	>0.00010
120	75 FTP	"	<0.00010	<0.00010	0.00010	<0.00010	0.00038	0.00024	0.00103	0.00022
121	75 FTP	0.091	0.00010	<0.00010	0.00022	<0.00010	0.00165	0.00038	>0.00202	0.00043
122	Idle (1)	"	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.00820]	[<0.00180]	[0.00680]	[<0.00180]
123	40 (1)	"	<0.00003	<0.00003	<0.00003	<0.00003	0.00008	<0.00003	0.00008	<0.00003
124	60 (2)	"	<0.00001	<0.00001	0.00002	<0.00001	0.00040	0.00002	>0.00009	0.00002
125	75 FTP	"	<0.00010	<0.00010	0.00020	<0.00010	0.00047	0.00025	>0.00101	0.00054

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* Bracketed numbers are idle emission rates of metals in gms/hour.

TABLE E-21

METAL DERIVED EXHAUST PARTICULATE EMISSIONS
TEST VEHICLE EQUIPPED WITH GRACE PELLETIZED OXIDATION CATALYST

EMISSION RATE, GMS/KM AS INDICATED METAL*

Test No.	Run Type	% Fuel Sulfur	Ca	Al	Zn	Cr	Fe	Cu	Ni	Pb
126	75 FTP	0.019	0.00011	0.00013	0.00168	<0.00010	0.00246	0.00019	0.00064	0.00063
127	Idle (1)	"	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.00260]	[<0.00180]	[<0.00180]	[<0.00180]
128	40 (1)	"	<0.00003	<0.00003	0.00014	<0.00003	0.00010	<0.00003	<0.00003	0.00005
129	60 (2)	"	0.00003	0.00003	0.00046	0.00001	>0.00046	0.00005	>0.00009	>0.00023
130	75 FTP	"	<0.00010	<0.00010	0.00047	<0.00010	0.00048	0.00019	0.00017	0.00020
131	75 FTP	0.110	<0.00010	<0.00010	0.00018	<0.00010	0.00172	<0.00010	<0.00010	0.00021
132	Idle (1)	"	[<0.00180]	[<0.00180]	[0.00300]	[<0.00180]	[0.00360]	[<0.00180]	[<0.00180]	[<0.00180]
133	40 (1)	"	<0.00003	<0.00003	<0.00003	<0.00003	0.00005	<0.00003	<0.00003	<0.00003
134	60 (2)	"	<0.00001	<0.00001	0.00003	<0.00001	0.00005	<0.00001	<0.00001	0.00003
135	75 FTP	"	<0.00010	<0.00010	0.00011	<0.00010	0.00076	0.00010	<0.00010	0.00012
136	75 FTP	0.091	<0.00010	0.00011	0.00058	<0.00010	0.00235	<0.00010	<0.00010	0.00035
137	Idle (1)	"	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.01100]	[<0.00180]	[<0.00180]	[0.00240]
138	40 (1)	"	<0.00003	<0.00003	0.00009	<0.00003	0.00026	<0.00003	<0.00003	0.00009
139	60 (2)	"	<0.00010	<0.00010	0.00004	<0.00010	0.00006	<0.00010	<0.00010	0.00002
140	75 FTP	"	<0.00010	<0.00010	<0.00010	<0.00010	0.00106	<0.00010	<0.00010	0.00021

---

* Bracketed numbers are idle emission rates in gms/hour.

TABLE E-22

METAL DERIVED EXHAUST PARTICULATE EMISSIONS
TEST VEHICLE EQUIPPED WITH UOP (2) MONOLITHIC OXIDATION CATALYST

EMISSION RATE, GMS/KM AS INDICATED METAL*

Test No.	Run Type	% Fuel Sulfur	Ca	Al	Zn	Cr	Fe	Cu	Ni	Pb
141	75 FTP	0.019	<0.00010	0.00010	0.00086	<0.00010	0.00493	0.00025	0.00019	
142	Idle (1)	"	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.00960]	[<0.00180]	[<0.00180]	[0.00180]
143	40 (1)	"	<0.00003	<0.00003	0.00005	<0.00003	0.00019	<0.00003	<0.00003	0.00006
144	60 (2)	"	<0.00001	0.00001	0.00023	<0.00001	0.00046	0.00003	0.00004	0.00015
145	75 FTP	"	<0.00010	<0.00010	0.00048	<0.00010	0.00012	0.00036	<0.00010	0.00040
146	75 FTP	0.110	<0.00010	0.00019	0.00142	<0.00010	0.00246	0.00032	0.00017	0.00067
147	Idle (1)	"	[<0.00180]	[0.00220]	[0.00200]	[<0.00180]	[0.00920]	[<0.00180]	[<0.00180]	[<0.00180]
148	40 (1)	"	<0.00003	<0.00003	0.00022	<0.00003	0.00027	<0.00003	<0.00003	0.00008
149	60 (2)	"	<0.00001	<0.00001	0.00003	<0.00001	0.00006	<0.00001	<0.00001	0.00002
150	75 FTP	"	<0.00010	<0.00010	0.00024	<0.00010	0.00214	0.00020	<0.00010	0.00024
151	75 FTP	0.091	<0.00010	<0.00010	0.00024	<0.00010	>0.00246	0.00030	<0.00010	0.00036
152	Idle (1)	"	[0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.01200]	[<0.00180]	[<0.00180]	[0.00300]
153	40 (1)	"	0.00003	<0.00003	0.00003	<0.00003	0.00019	<0.00003	<0.00003	0.00005
154‡	60 (2)	"	---	---	---	---	---	---	---	---
155	75 FTP	"	<0.00010	<0.00010	0.00013	<0.00010	0.00236	0.00026	<0.00010	0.00030

---

* Bracketed numbers are idle emission rates in gms/hour.

‡ Filter badly fragmented.

TABLE E-23

METAL DERIVED EXHAUST PARTICULATE EMISSION RATES
TEST VEHICLE EQUIPPED WITH AIR PRODUCTS PELLETIZED OXIDATION CATALYST

EMISSION RATE, GMS/KM AS INDICATED METAL*

Test No.	Run Type	% Fuel Sulfur	Ca	Al	Zn	Cr	Fe	Cu	Ni	Pb
156	75 FTP	0.019	<0.00010	0.00028	0.00111	<0.00100	>0.00246	0.00025	<0.00010	0.00065
157	Idle (1)	"	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.00660]	[<0.00180]	[<0.00180]	[<0.00180]
158	40 (1)	"	<0.00003	<0.00003	<0.00003	<0.00003	0.00010	<0.00003	<0.00003	<0.00003
159	60 (2)	"	<0.00001	<0.00001	0.00004	<0.00001	0.00015	<0.00001	0.00001	0.00004
160	75 FTP	"	<0.00010	<0.00010	0.00024	<0.00010	0.00116	0.00017	<0.00010	0.00026
161	75 FTP	0.110	<0.00010	<0.00010	0.00022	<0.00010	0.00154	0.00028	0.00016	0.00048
162	Idle (1)	"	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]
163	40 (1)	"	<0.00003	0.00005	0.00019	0.00003	>0.00068	0.00007	0.00008	0.00015
164	60 (2)	"	0.00001	0.00001	0.00001	>0.00009	0.00046	<0.00010	>0.00009	0.00001
165	75 FTP	"	<0.00010	<0.00010	0.00012	<0.00010	0.00235	<0.00010	<0.00010	0.00015
166	75 FTP	0.091	<0.00010	<0.00010	0.00019	<0.00010	0.00493	0.00015	<0.00010	0.00030
167	Idle (1)	"	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.01720]	[<0.00180]	[<0.00180]	[<0.00180]
168	40 (1)	"	<0.00003	<0.00003	<0.00003	<0.00003	0.00026	<0.00003	<0.00003	<0.00003
169	60 (2)	"	0.00001	<0.00001	0.00005	<0.00001	>0.00023	0.00001	0.00001	0.00004
170	75 FTP	"	<0.00010	<0.00010	0.00012	<0.00010	0.00246	<0.00010	<0.00010	0.00032

---

* Bracketed numbers are idle emission rates in gms/hour.

TABLE E-24

METAL DERIVED EXHAUST PARTICULATE EMISSION RATES
TEST VEHICLE EQUIPPED WITH ENGELHARD PELLETIZED OXIDATION CATALYST
AFTER CONDITIONING ON 0.091% SULFUR FUEL FOR 6400 KILOMETRES ON FEDERAL DURABILITY CYCLE

EMISSION RATE, GMS/KM AS INDICATED METAL*

Test No.	Run Type	% Fuel Sulfur	Ca	Al	Zn	Cr	Fe	Cu	Ni	Pb
171	75 FTP	0.019	<0.00010	0.00017	0.00045	0.00021	>0.00246	0.00040	0.00029	0.00104
172	Idle (1)	"	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.00300]	[<0.00180]	[<0.00180]	[<0.00180]
173	40 (1)	"	<0.00003	<0.00003	<0.00003	<0.00003	0.00008	<0.00003	<0.00003	<0.00003
174	60 (2)	"	<0.00001	<0.00001	0.00003	<0.00001	0.00009	<0.00001	<0.00001	0.00002
175	75 FTP	"	<0.00010	<0.00010	<0.00010	<0.00010	0.00125	0.00016	<0.00010	0.00016

---

* Bracketed numbers are idle emission rates in gms/hour.

TABLE E-25

SULFATE EMISSIONS
UNEQUIPPED MILEAGE ACCUMULATION VEHICLE

Test No.	% Fuel Sulfur	Run Type	Sulfate Emission Rate* gms/km
1	0.019	75 FTP	0.002
2	"	Idle (1)	[0.005]
3	"	40 (1)	0.001
4	"	70 (2)	0.002
5	"	75 FTP	0.003
6	0.110	75 FTP	0.003
7	"	Idle (1)	[0.027]
8	"	40 (1)	<0.001
9	"	70 (2)	0.005
10	"	75 FTP	0.002
11	0.091	"	0.002
12	"	Idle (1)	[0.028]
13	"	40 (1)	<0.001
14	"	70 (2)	0.003
15	"	75 FTP	<0.001

---

* Numbers in brackets are idle emission rates in gms/hr.

TABLE E-26

SULFATE EMISSIONS
UNEQUIPPED TEST VEHICLE

Test No.	% Fuel Sulfur	Run Type	Sulfate Emission Rate* gms/km
16	0.019	75 FTP	0.001
17	"	Idle (1)	[0.021]
18	"	40 (1)	<0.001
19	"	70 (2)	0.001
20	"	75 FTP	0.001
21	0.110	75 FTP	0.003
22	"	Idle (1)	[0.021]
23	"	40 (1)	<0.001
24	"	70 (2)	0.002
25	"	75 FTP	0.002
26	0.091	75 FTP	0.002
27	"	Idle (1)	[0.024]
28	"	40 (1)	0.001
29	"	70 (2)	0.002
30	"	75 FTP	0.002

---

* Numbers in brackets are idle emission rates in gms/hr.

TABLE E-27

SULFATE EMISSIONS
TEST VEHICLE EQUIPPED WITH ENGELHARD MONOLITHIC OXIDATION CATALYST

Test No.	% Fuel Sulfur	Run Type	Sulfate Emission Rate* gms/km
36	0.019	75 FTP	0.002
37	"	Idle (1)	[0.103]
38	"	40 (1)	0.012
39	"	70 (2)	0.010
40	"	75 FTP	0.004
41	0.110	75 FTP	0.060
42	"	Idle (1)	[0.048]
43	"	40 (1)	0.101
44	"	70 (2)	0.055
45	"	75 FTP	0.053
46	0.091	75 FTP	0.087
47	"	Idle (1)	[0.028]
48	"	40 (1)	0.076
49	"	70 (2)	0.057
50	"	75 FTP	0.050

---

* Numbers in brackets are idle emission rates in gms/hr.

TABLE E-28

SULFATE EMISSIONS TEST VEHICLE EQUIPPED WITH ENGELHARD PELLETIZED OXIDATION CATALYST

Test No.	% Fuel Sulfur	Run Type	Sulfate Emission Rate* gms/km
51	0.019	75 FTP	0.003
52	"	Idle	[0.022]
53	"	40 (1)	0.001
54	"	70 (2)	0.027
55	"	75 FTP	0.002
56	0.110	75 FTP	0.008
57	"	Idle (1)	[0.052]
58	"	40 (1)	0.104
59	"	70 (2)	0.103
60	"	75 FTP	0.029
61	0.091	75 FTP	0.016
62	"	Idle (1)	[0.0]
63	"	40 (1)	0.078
64	"	70 (2)	0.046
65	"	75 FTP	0.006

---

* Numbers in brackets are idle emission rates in gms/hr.

TABLE E-29

SULFATE EMISSIONS
TEST VEHICLE EQUIPPED WITH UOP(1)
MONOLITHIC OXIDATION CATALYST

Test No.	% Fuel Sulfur	Run Type	Sulfate Emission Rate* gms/km
66	0.019	75 FTP	0.003
67	"	Idle (1)	[0.021]
68	"	40 (1)	0.013
69	"	70 (2)	0.011
70	"	75 FTP	0.001
71	0.110	75 FTP	0.022
72	"	Idle (1)	[0.011]
73	"	40 (1)	0.183
74	"	70 (2)	0.065
75	"	75 FTP	0.027
76	0.091	75 FTP	0.033
77	"	Idle (1)	[0.034]
78	"	40 (1)	0.165
79	"	70 (2)	0.061
80	"	75 FTP	0.008

---

* Numbers in brackets are idle emission rates in gms/hr.

TABLE E-30

SULFATE EMISSIONS
TEST VEHICLE EQUIPPED WITH MATTHEY BISHOP MONOLITHIC OXIDATION CATALYST

Test No.	% Fuel Sulfur	Run Type	Sulfate Emission Rate* gms/km
81	0.019	75 FTP	0.003
82	"	Idle (1)	[0.0]
83	"	40 (1)	0.006
84	"	60 (2)	0.010
85	"	75 FTP	0.003
86	0.110	75 FTP	0.032
87	"	Idle (1)	[0.0]
88	"	40 (1)	0.055
89	"	60 (2)	0.068
90	"	75 FTP	0.016
91	0.091	75 FTP	0.024
92	"	Idle (1)	[0.0]
93	"	40 (1)	0.043
94	"	60 (2)	0.058
95	"	75 FTP	0.015

---

* Numbers in brackets are idle emission rates in gms/hr.

TABLE E-31

SULFATE EMISSIONS TEST VEHICLE EQUIPPED WITH GRACE NO_x REDUCTION CATALYST*

Test No.	% Fuel Sulfur	Run Type	Sulfate Emission Rate** gms/km
96	0.019	75 FTP	0.002
97	"	Idle (1)	[0.000]
98	"	40 (1)	0.002
99	"	60 (2)	0.001
100	"	75 FTP	0.001
101	0.110	75 FTP	0.004
102	"	Idle (1)	[0.000]
103	"	40 (1)	0.065
104	"	60 (2)	0.027
105	"	75 FTP	0.005
106	0.091	75 FTP	0.001
107	"	Idle (1)	[0.000]
108	"	40 (1)	0.043
109	"	60 (2)	0.024
110	"	75 FTP	<0.001

---

* Exhaust gas recycle and air pump disconnected.

** Numbers in brackets are idle emission rates in gms/hr.

TABLE E-32

SULFATE EMISSIONS
TEST VEHICLE EQUIPPED WITH
GOULD NO_x REDUCTION CATALYST*

Test No.	% Fuel Sulfur	Run Type	Sulfate Emission Rate** gms/km
111	0.019	75 FTP	0.002
112	"	Idle (1)	[0.000]
113	"	40 (1)	0.002
114	"	60 (2)	0.006
115	"	75 FTP	<0.001
116	0.110	75 FTP	<0.001
117	"	Idle (1)	[0.000]
118	"	40 (1)	0.044
119	"	60 (2)	0.039
120	"	75 FTP	0.003
121	0.091	75 FTP	0.001
122	"	Idle (1)	[0.000]
123	"	40 (1)	0.034
124	"	60 (2)	0.040
125	"	75 FTP	0.000

---

* Exhaust gas recycle and air pump disconnected.

** Numbers in brackets are idle emission rates in gms/hr.

TABLE E-33

SULFATE EMISSIONS
TEST VEHICLE EQUIPPED WITH GRACE PELLETIZED OXIDATION CATALYST

Test No.	% Fuel Sulfur	Run Type	Sulfate Emission Rate* gms/km
126	0.019	75 FTP	0.002
127	"	Idle (1)	0.000
128	"	40 (1)	0.006
129	"	60 (2)	0.019
130	"	75 FTP	0.007
131	0.110	75 FTP	0.009
132	"	Idle (1)	0.000
133	"	40 (1)	0.088
134	"	60 (2)	0.146
135	"	75 FTP	0.034
136	0.091	75 FTP	0.010
137	"	Idle (1)	[0.047]
138	"	40 (1)	0.067
139	"	60 (2)	0.096
140	"	75 FTP	0.026

---

* Numbers in brackets are idle emission rates in gms/hr.

TABLE E-34

SULFATE EMISSIONS
TEST VEHICLE EQUIPPED WITH
UOP(2) MONOLITHIC OXIDATION CATALYST

Test No.	% Fuel Sulfur	Run Type	Sulfate Emission Rate* gms/km
141	0.019	75 FTP	0.006
142	"	Idle (1)	[0.025]
143	"	40 (1)	0.015
144	"	60 (2)	0.024
145	"	75 FTP	0.008
146	0.110	75 FTP	0.032
147	"	Idle (1)	---
148	"	40 (1)	0.176
149	"	60 (2)	0.113
150	"	75 FTP	0.090
151	0.091	75 FTP	0.078
152	"	Idle (1)	[0.022]
153	"	40 (1)	0.160
154	"	60 (2)	0.110
155	"	75 FTP	0.052

---

* Numbers in brackets are idle emission rates in gms/hr.

TABLE E-35

SULFATE EMISSIONS
TEST VEHICLE EQUIPPED WITH AIR PRODUCTS
PELLETIZED OXIDATION CATALYST

Test No.	% Fuel Sulfur	Run Type	Sulfate Emission Rate* gms/km
156	0.019	75 FTP	0.014
157	"	Idle (1)	[0.030]
158	"	40 (1)	0.012
159	"	60 (2)	0.017
160	"	75 FTP	0.004
161	0.110	75 FTP	0.032
162	"	Idle (1)	[0.033]
163	"	40 (1)	0.096
164	"	60 (2)	
165	"	75 FTP	0.054
166	0.091	75 FTP	0.023
167	"	Idle (1)	[0.394]
168	"	40 (1)	
169	"	60 (2)	0.103
170	"	75 FTP	0.075

---

* Numbers in brackets are idle emission rates in gms/hr.

TABLE E-36

SULFATE EMISSIONS AFTER STORAGE

Test Vehicle Equipped With Engelhard
Pelletized Oxidation Catalyst After Conditioning
Catalyst for 3200 km on Federal Durability Cycle

Test No.	% Fuel Sulfur	Run Type	Sulfate Emission Rate gms/km
171	0.019	75 FTP	0.044
172	"	Idle (1)	---
173	"	40 (1)	0.119
174	"	60 (2)	0.103
175	"	75 FTP	0.100

E.2 Precision of Total Particulate Emission Measurements

As previously discussed in Section II.2.2.4, two parallel probes coupled to appropriate filters are required to serve as internal checks on the particulate sampling system. Reliable, accurate exhaust particulate emission rates can be obtained only if close agreement between parallel filter increases are consistently obtained.

Regression of 172 of the program runs showed the following filter correspondence:

$\Delta W_A = 0.98\ \Delta W_B$ where

ΔW_A and ΔW_B are the weight gains of parallel filters A and B respectively.

APPENDIX F

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